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Locating and Estimating Air Emissions from Sources of Chlorobenzenes

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16. ABSTRACT

To assist groups interested in inventorying air emissions of various potentially toxic substances, EPA is preparing a series of documents such as this to compile available information on sources and emissions of these substances. This document deals specifically with Chlorobenzenes. Its intended audience includes Federal, State and local air pollution personnel and others interested in locating potential emitters of Chlorobenzenes and in making gross estimates of air emissions therefrom.

This document presents information on 1) the types of sources that may emit Chlorobenzenes, 2) process variations and release points that may be expected within these sources, and 3) available emissions information indicating the potential for Chlorobenzenes release into the air from each operation.

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Locating And Estimating Air Emissions From Sources Of Chlorobenzenes

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September 1986

Locating And Estimating Air Emissions From Sources Of Chlorobenzenes

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office Of Air And Radiation
Office Of Air Quality Planning And Standards
Research Triangle Park, North Carolina 27711

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SECTION 1

PURPOSE OF DOCUMENT

EPA, States and local air pollution control agencies are becoming increasingly aware of the presence of substances in the ambient air that may be toxic at certain concentrations. This awareness, in turn, has led to attempts to identify source/receptor relationships for these substances and to develop control programs to regulate emissions. Unfortunately, very little information is available on the ambient air concentrations of these substances or on the sources that may be discharging them to the atmosphere.

To assist groups interested in inventorying air emissions of various potentially toxic substances, EPA is preparing a series of documents such as this that compiles available information on sources and emissions of these substances. This document specifically deals with chlorobenzenes, namely, monochlorobenzene, dichlorobenzenes, trichlorobenzenes, and hexachlorobenzene. Its intended audience includes Federal, State and local air pollution personnel and others who are interested in locating potential emitters of chlorobenzenes and making preliminary estimates of air emissions therefrom.

Because of the limited amounts of data available on chlorobenzene emissions, and since the configuration of many sources will not be the same as those described herein, this document is best used as a primer to inform air pollution personnel about 1) the types of sources that may emit chlorobenzenes, 2) process variations and release points that may be expected within these sources, and 3) available emissions information indicating the potential for chlorobenzenes to be released into the air from each operation.

The reader is strongly cautioned against using the emissions information contained in this document to try to develop an exact assessment of emissions from any particular facility. Since insufficient data are available to develop statistical estimates of the accuracy of these emission factors, no estimate can be made of the error that could result when these factors are used to calculate emissions from any given facility. It is possible, in some extreme cases, that orders-of-magnitude differences could result between actual and calculated emissions, depending on differences in source configurations, control equipment and operating practices. Thus, in situations where an accurate assessment of chlorobenzene emissions is necessary, source-specific information should be obtained to confirm the existence of particular emitting operations, the types and effectiveness of control measures, and the impact of operating practices. A source test and/or material balance should be considered as the best means to determine air emissions directly from an operation.

SECTION 2

OVERVIEW OF DOCUMENT CONTENTS

As noted in Section 1, the purpose of this document is to assist Federal, State and local air pollution agencies and others who are interested in locating potential air emitters of chlorobenzenes and making gross estimates of air emissions therefrom. Because of the limited background data available, the information summarized in this document does not and should not be assumed to represent the source configuration or emissions associated with any particular facility.

This section provides an overview of the contents of this document. It briefly outlines the nature, extent and format of the material presented in the remaining sections of this report.

Section 3 of this document provides a brief summary of the physical and chemical characteristics of chlorobenzenes, commonly occurring forms and an overview of their production and uses. A chemical use tree summarizes the quantities of chlorobenzenes consumed in various end use categories in the United States. This background section may be useful to someone who needs to develop a general perspective on the nature of the substances and where they are manufactured and consumed.

Section 4 of this document focuses on major industrial source categories that may discharge air emissions containing chlorobenzenes. This section discusses the manufacture of chlorobenzenes, their use as industrial feedstocks, and their use as individual commercial products. For each major industrial source category described in Section 4, example process descriptions and flow diagrams are given, potential emission points are identified, and available emission factor estimates are presented that show the potential for chlorobenzene emissions before and after controls employed by industry. Individual companies are named that are reported to be involved with either the production or use of chlorobenzenes, based primarily on trade publications.

The final section of this document summarizes available procedures for source sampling and analysis of chlorobenzenes. Details are not prescribed nor is any EPA endorsement given or implied to any of these sampling and analysis procedures. At this time, EPA generally has not evaluated these methods. Consequently, this document merely provides an overview of applicable source sampling procedures, citing references for those interested in conducting source tests.

This document does not contain any discussion of health or other environmental effects of chlorobenzenes, nor does it include any discussion of ambient air levels or ambient air monitoring techniques.

Comments on the contents or usefulness of this document are welcomed, as is any information on process descriptions, operating practices, control measures and emissions information that would enable EPA to improve its contents. All comments should be sent to:

Chief, Noncriteria Emissions Section (MD-14)
Air Management Technology Branch
U.S. Environmental Protection Agency
Research Triangle Park, N.C. 27711

SECTION 3

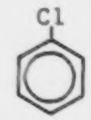
BACKGROUND

NATURE OF POLLUTANT

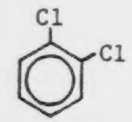
The chlorinated derivatives of benzene, $C_6H_{(6-x)}Cl_x$, form a group of stable, colorless, pleasant smelling compounds. The six hydrogen atoms of the benzene ring can be substituted by chlorine, forming twelve chlorine compounds:

- monochlorobenzene
- o-dichlorobenzene
- p-dichlorobenzene
- m-dichlorobenzene
- 1,2,3-trichlorobenzene
- 1,2,4-trichlorobenzene
- 1,2,5-trichlorobenzene
- 1,2,3,4-tetrachlorobenzene
- 1,3,4,5-tetrachlorobenzene
- 1,2,4,5-tetrachlorobenzene
- pentachlorobenzene
- hexachlorobenzene

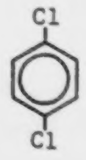
Only the mono-, di-, and trichlorobenzenes have important industrial applications. Thus, this report deals with air emissions of the following chlorinated derivatives of benzene:



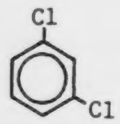
monochlorobenzene



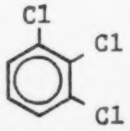
ortho-dichlorobenzene



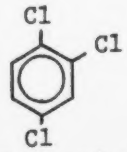
para-dichlorobenzene



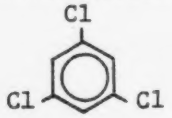
meta-dichlorobenzene



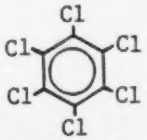
1,2,3-trichlorobenzene



1,2,4-trichlorobenzene



1,3,5-trichlorobenzene



hexachlorobenzene

Although it has no current commercial applications, hexachlorobenzene is also included due to toxicity considerations, its past usage, and generation as a byproduct in other manufacturing processes. Synonyms and trade names for these chlorinated benzenes are given in Table 1.

The physical properties of the industrially significant chlorobenzenes are listed in Table 2. Vapor pressure as a function of temperature is correlated by the Antoine equation:

$$\log_{10} P\ (\text{kPa}) = A - B/(T+C) - 0.875097,$$

where T is the temperature in °C and A, B, and C are the Antoine constants. Antoine constants found in the literature are listed in Table 2.

Monochlorobenzene is almost insoluble in water. If it accumulates in raw water systems, it tends to sink. Because of its comparatively high volatility, there may be a greater tendency for monochlorobenzene to accumulate in still lake waters rather than fast moving streams and rivers.[1]

Monochlorobenzene has a high solubility in nonpolar solvents, and all chlorinated derivatives of benzene are soluble in lipids. Partition coefficient data for chlorinated benzenes show an increase in partition coefficient with an increase in the degree of chlorination. In general, a positive correlation exists between partition coefficient and degree of bioaccumulation.

Ortho- and meta-dichlorobenzene are neutral, mobile, colorless liquids with similar and characteristic odors. Para-dichlorobenzene is a pleasant smelling white crystalline solid. The crystals readily sublime at room temperature. Solubilities of the dichlorobenzenes are

TABLE 1: SYNONYMS AND TRADE NAMES FOR CHLORINATED BENZENES[1,2]

Monochlorobenzene:	benzene chloride; chlorobenzene; chlorobenzol; phenyl chloride; MCB; NCI-C54886
o-Dichlorobenzene:	orthodichlorobenzene; ortho-dichlorobenzene; ortho-dichlorobenzol; 1,2-dichlorobenzene; ODB; ODCB; Dizene®; Chloroben®; Dowtherm® E; "Special termite fluid"; Termitekil; Dilatin DB
p-Dichlorobenzene:	paradichlorobenzene; para-dichlorobenzene; para-dichlorobenzol; 1,4-dichlorobenzene; PDB; PDCB; Di-chloricide®; Paracide®; Paradi®; Paradow®; Paramoth®; Santochlor®; Parazene; Paranuggets; paraCrystals; p-chlorophenyl chloride; Evola; Persia-Perazol
m-Dichlorobenzene:	metadichlorobenzene; meta-dichlorobenzol; meta-dichlorobenzene; 1,3-dichlorobenzene; m-phenylenedichloride
1,2,3-Trichlorobenzene:	1,2,3-trichlorobenzol; 1,2,3-TCB; 1,2,6-trichlorobenzene; vic-trichlorobenzene
1,2,4-Trichlorobenzene:	1,2,4-trichlorobenzol; 1,2,4-TCB; asym-trichlorobenzene; Hostetex L-Pec
1,3,5-Trichlorobenzene:	1,3,5-trichlorobenzol; 1,3,5-TCB; sym-trichlorobenzene; s-trichlorobenzene; TCBA
Hexachlorobenzene:	Amatin; Anticarie; Bunt-Cure; Bunt-No-More; Co-op Hexa; Granox NM; HCB; HEXA C.B.; Julin's Carbon Chloride; No Bunt; No Bunt 40; No Bunt 80; No Bunt Liquid; pentachlorophenyl chloride; perchlorobenzene; phenylperchloryl; Sanocide; Smut-Go; Snieciotox

TABLE 2. PROPERTIES OF INDUSTRIALLY SIGNIFICANT CHLOROBENZENES[1,3,4,5]

	MCB	o-DCB	p-DCB	m-DCB	1,2,4-TCB	1,3,5-TCB	1,2,3-TCB	HCB
Chemical Abstract Service Registry Number	108-90-7	95-50-1	106-46-7	541-73-1	120-82-1	108-70-3	87-61-6	118-74-1
Chemical Formula								
Molecular Weight	112.56	147.0	147.0	147.0	181.5	181.5	181.5	284.76
Molecular Formula	C_6H_5Cl	$C_6H_4Cl_2$	$C_6H_4Cl_2$	$C_6H_4Cl_2$	$C_6H_3Cl_3$	$C_6H_3Cl_3$	$C_6H_3Cl_3$	C_6Cl_6
Physical Properties								
Physical State at STP	liquid -colorless	liquid -colorless	monoclinic crystals (volatile)	liquid -colorless	liquid	solid crystalline	solid crystalline	solid crystalline
Boiling Point (at 760mm)	131.7°C	180.5°C	174.12°C	173.0°C	213.0°C	208.0°C	218.0°C	3229°C
Melting Point	-45.5°C	-17.0°C	53.5°C	-24.7°C	16.6°C	63.0°C	52.4°C	230°C
Density (g/ml) (at 20°C/4°C)	1.1058	1.305	1.288	1.288	1.46	---	1.69	1.57 (at 23°C)
Vapor Pressure (mm Hg at 25°C)	11.8	1.28	1.89	0.4	0.29	0.15	---	1.68×10^{-5}
Antoine Constants								
A	16.0676	16.2799	16.1135	16.8173	---	---	---	---
B	3295.12	3798.23	3626.83	4104.13	---	---	---	---
C	-55.60	-59.84	-64.64	-43.15	---	---	---	---
Vapor Density	3.88	5.05	---	---	---	---	---	---
Solubility in Water	insoluble	slightly (0.145g/1 H_2O)	nearly insol. (0.079g/1 H_2O)	insoluble	insoluble	insoluble	insoluble	insoluble
Log Partition Coefficient (Octanol/H_2O)	2.84	3.38	3.39	---	---	---	---	---
Atmospheric Reactivity								
Transformation Products								
Reactivity Toward OH	1/3 Butane	1/2 Butane	1/2 Butane	---	---	---	---	---
Reactivity Toward O_3	No reaction	5% Propylene	5% Propylene	---	---	---	---	---

similar to those of monochlorobenzene, and the dichlorobenzenes also form a number of azeotropes. All three dichlorinated compounds are combustible.

The trichlorinated benzenes are white crystalline solids except for 1,2,4-trichlorobenzene which is a colorless liquid. Solubilities are similar, with insolubility in water, generally good solubility in alcohol, ether, benzene, and chloroform, and relatively high lipid solubility.[1]

Hexachlorobenzene is a colorless crystalline solid at normal temperatures shown to degrade slowly in the environment. Although insoluble in water, it is slightly soluble in cold alcohol and soluble in benzene, chloroform, and ethyl ether. Rapid sublimation of the crystals occurs in the temperature range of 0° to 30°C.[4]

As a group, chlorobenzenes are much less reactive than the corresponding chlorinated derivatives of alkyl compounds and are similar in reactivity to the vinyl chlorides. They are very stable to nucleophilic attack due to resonance in the molecule resulting in a shortening of the carbon chlorine bond distance and an increase in bond strength.

At room temperature and pressure, chlorobenzenes are not attacked by air, moisture, or light. They are not affected by steam, prolonged boiling with aqueous or alcoholic ammonia, other alkalis, hydrochloric acid, or dilute sulfuric acid. Hydrolysis takes place at elevated temperatures in the presence of a catalyst to form phenols.

Chlorobenzenes are subject to attack by hot concentrated sulfuric acid to form a chlorobenzene-p-sulfonic acid. Nitric acid will react with chlorobenzenes at the meta and para positions on the ring to form chloronitrobenzenes at -30° to 0°C. At higher temperatures, the nitration will either proceed further to form a dinitrochloro compound, chloronitrophenol, or a nitrophenol.[1]

Chlorobenzenes are attacked by electrophilic agents. Substitution for monochlorobenzene is predominantly para; with some ortho substitution. The higher chlorinated benzenes tend to resist electrophilic substitution but can be substituted under extreme conditions.

Chlorobenzenes also undergo some free radical reactions. Formation of organometallic compounds (originals, aryl-lithium compounds) provides a useful route to many organic intermediates. Photochemical transformations occur on irradiation of chlorinated benzenes, which are much less stable to radiation than benzene. On ultraviolet irradiation or pulse hydrolysis in solution, chlorobenzenes may polymerize to biphenyls, chloronaphthalenes, or other more complex products.

Because of the wide variety of chemical reactions that chlorobenzenes can undergo, chlorinated benzenes can be used as reactants in numerous commercial processes to produce a wide variety of products.

OVERVIEW OF PRODUCTION AND USES

Twelve chlorinated benzenes can be formed by replacing some or all of the hydrogen atoms of benzene with chlorine atoms. With the exceptions of 1,3-dichlorobenzene, 1,3,5-trichlorobenzene, and 1,2,3,5-tetrachlorobenzene, they are produced readily by chlorinating benzene in the presence of a Friedel-Crafts catalyst. The usual catalyst is ferric chloride, either as such or generated in situ by exposing a large surface of iron to the liquid being chlorinated. Each compound, except hexachlorobenzene, can be chlorinated further; hence, the product is always a mixture of chlorinated benzenes. Pure compounds are obtained by distillation and crystallization.

Chlorobenzenes were synthesized first in the middle of the nineteenth century. The first direct chlorination of benzene was reported in 1905. Commercial production was initiated in 1909 by the former United Alkali Company in England. In 1915, the Hooker Electrochemical Company began operation of its first chlorobenzenes plant in the United States at Niagara Falls. The Dow Chemical Company also started its U.S. production of chlorobenzenes in 1915.[6]

Currently, there are five domestic producers of chlorobenzenes at the same number of locations. In 1984, production capacity for monochlorobenzene was 157 x 10^3 Mg, for o-dichlorobenzene it was 35 x 10^3 Mg, and for p-dichlorobenzene, 54 x 10^3 Mg.[7,8,9] Few data are available on production of more highly chlorinated benzenes.

Processes for the manufacture of chlorobenzenes have developed over a long period of time, with various chemistry and product separation methods being used. The process currently used by industry is direct chlorination of benzene in the presence of $FeCl_3$ catalyst to produce monochlorobenzene. The monochlorobenzene reacts with the remaining chlorine to form dichlorobenzenes. Hydrogen chloride is a by-product in both reactions. Along with the two major isomers of dichlorobenzene, ortho- and para-, a very small amount of the meta-isomer is formed. As chlorination is continued, tri-, tetra-, penta-, and hexachlorobenzenes are formed. Usually, trichlorobenzene is the only one of the more highly chlorinated products found in significant amounts. The degree of chlorination of benzene can be controlled by the choice of the catalyst, temperature, and benzene:chlorine ratio in the reactor feed. Hydrogen chloride, a byproduct of the reaction, is processed under anhydrous conditions before it is absorbed in water. The reaction and the recovery operations, in most cases, are continuous.

Chlorobenzene production plants vary in capacity from 10 million to 160 million kg/year. In general, with the decreasing use of monochlorobenzene, the thrust of commercial chlorobenzene producers has been toward maximizing dichlorobenzene and trichlorobenzene capacity.

Demand for monochlorobenzene as a feedstock comes mostly from the synthetic organic chemical industry. Accordingly, since the manufacturing process is simple, it is often manufactured in the same plant in which it is consumed. The two major markets for monochlorobenzene have been in the manufacture of phenol and o- and p- nitrochlorobenzenes. Continued growth in these markets is doubtful, since cumene is now primarily used as a raw material for phenol manufacture.[10] Other feedstock uses include use in the manufacture of diphenyl oxide, rubber intermediates, and DDT.

o-Dichlorobenzene is used primarily in organic synthesis of 3,4-dichloroaniline which is used as an intermediate in the production of pesticides. Demand for o-dichlorobenzene as a solvent carrier in the manufacture of toluene diisocyanate for polyurethane manufacture has increased, and is expected to grow faster than any other use. It also is used as a solvent in paint removers and engine cleaners, in de-inking solvents, and in dye manufacture.[12]

p-Dichlorobenzene is used extensively as a moth repellent. Its vapor pressure and pleasant odor make it very suitable for this application. It is predicted that this use will hold steady, in addition to its use as a space odorant. Moderate growth is expected for its use in the manufacture of polyphenylene sulfide resins.[13] It is also used in the production of dye intermediates, insecticides, pharmaceuticals, and as an extreme pressure lubricant.[11]

1,2,4-Trichlorobenzene is primarily used in textile dyeing operations as a dye carrier but also finds uses in production of herbicides and dyes. It has also been employed as a high melting point product solvent, degreasing agent, termite control agent, synthetic transformer oil, lubricant, heat transfer medium and dielectric fluid.[11]

m-DCB, 1,2,3-TCB, and 1,3,5-TCB, and all three tetrachlorobenzenes are not discussed here due to their limited production and use.

Hexachlorobenzene is no longer produced or imported into the United States for commercial usage. Formerly, hexachlorobenzene was used as an active ingredient in fungicidal preparations, but this use has been nearly eliminated due to the cancellation of registry of HCB-containing fungicides. Currently, hexachlorobenzene is formed as a process waste byproduct during the manufacture of specific chlorinated solvents and pesticides.[14,15]

A summary of current uses of each of the industrially significant chlorobenzenes is presented in Figure 1, along with the percentage of total product devoted to each use. Since hexachlorobenzene has no current uses, a summary of past uses is presented in Figure 2.

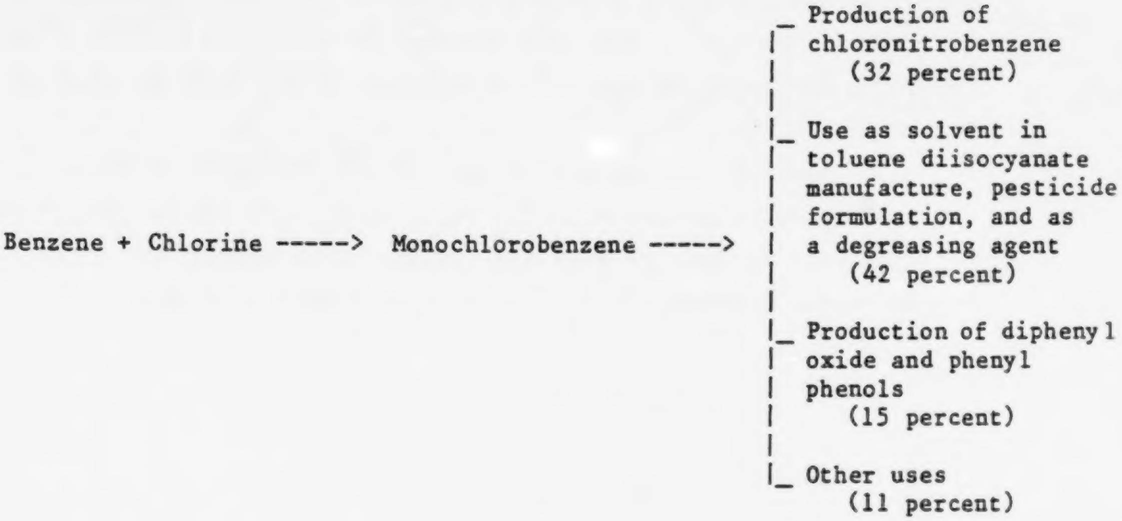
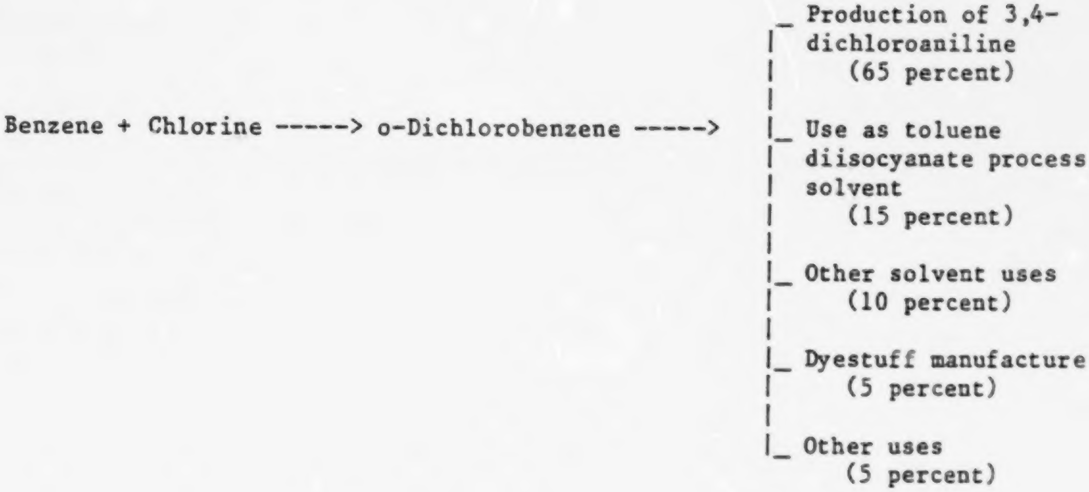

Benzene + Chlorine -----> Monochlorobenzene ----->
Production of chloronitrobenzene (32 percent)
Use as solvent in toluene diisocyanate manufacture, pesticide formulation, and as a degreasing agent (42 percent)
Production of diphenyl oxide and phenyl phenols (15 percent)
Other uses (11 percent)

Figure 1. Uses of chlorinated benzenes.[10]



Benzene + Chlorine -----> o-Dichlorobenzene ----->

- Production of 3,4-dichloroaniline (65 percent)
- Use as toluene diisocyanate process solvent (15 percent)
- Other solvent uses (10 percent)
- Dyestuff manufacture (5 percent)
- Other uses (5 percent)

Figure 1. (continued) Uses of chlorinated benzenes.[12]

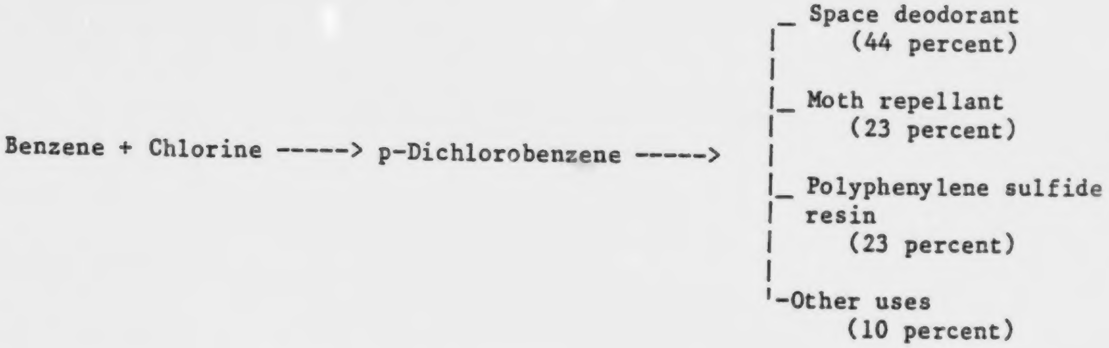

Benzene + Chlorine -----> p-Dichlorobenzene ----->
Space deodorant (44 percent)
Moth repellant (23 percent)
Polyphenylene sulfide resin (23 percent)
Other uses (10 percent)

Figure 1. (continued) Uses of chlorinated benzenes.[93]

```
                                                               _ Use as a dye carrier
                                                              |     (46 percent)
                                                              |
Benzene + Chlorine ---> 1,2,4-Trichlorobenzene--->            |_ Production of
                                                              |  herbicides, including
                                                              |  dicamba
                                                              |     (29 percent)
                                                              |
                                                              |_ Other uses
                                                                    (25 percent)
```

Figure 1. (continued) Uses of chlorinated benzenes.[11]

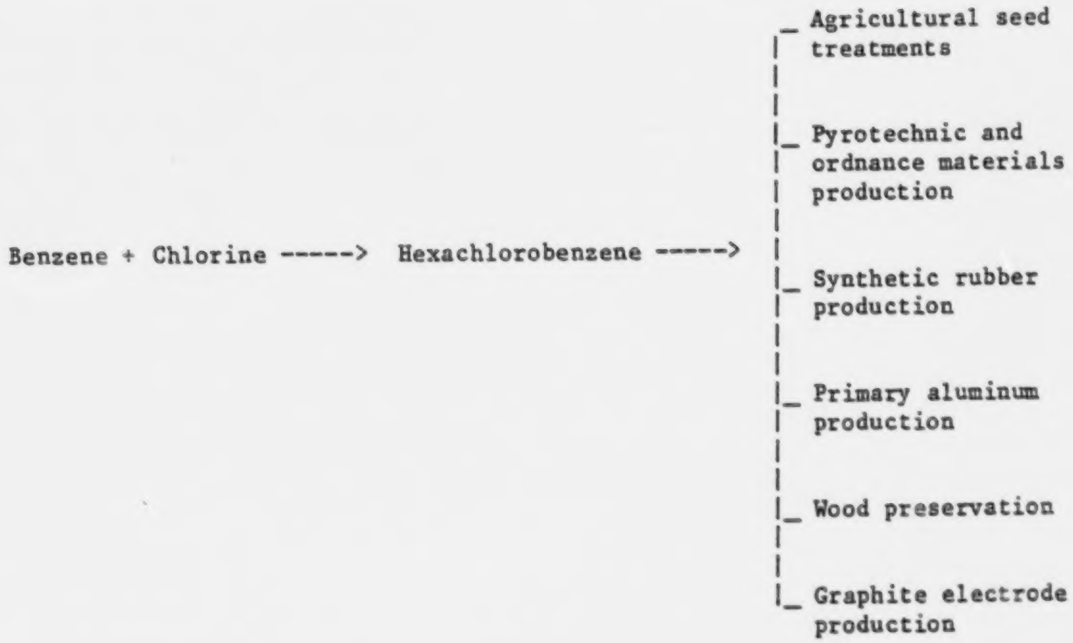

Benzene + Chlorine -----> Hexachlorobenzene ----->
Agricultural seed treatments
Pyrotechnic and ordnance materials production
Synthetic rubber production
Primary aluminum production
Wood preservation
Graphite electrode production

Figure 2. Past uses of hexachlorobenzene.[16]

SECTION 4

EMISSION SOURCES OF CHLOROBENZENES

This section discusses chlorobenzene emissions from direct sources such as the production of monochlorobenzene, dichlorobenzenes, trichlorobenzenes, and hexachlorobenzene; production of chemicals which use chlorobenzenes as feedstocks; and direct use of the chemicals. Generation of hexachlorobenzene as a byproduct in other manufacturing processes is also discussed. Process descriptions, uses, and related emissions are discussed for the following chlorobenzenes:

- Monochlorobenzene
- o-dichlorobenzene
- p-dichlorobenzene
- m-dichlorobenzene
- 1,2,3-trichlorobenzene
- 1,2,4-trichlorobenzene
- 1,3,5-trichlorobenzene
- hexachlorobenzene

Due to limited current uses, tetrachlorobenzenes and pentachlorobenzenes are considered industrially insignificant and are not discussed.

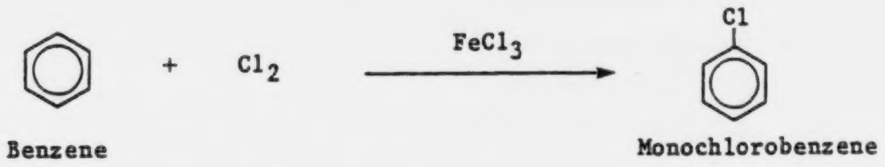
CHLOROBENZENE PRODUCTION

The general process by which chlorobenzenes are manufactured is direct chlorination of the benzene ring in the presence of a catalyst to form monochlorobenzene (MCB) and o- and p-dichlorobenzenes. By the manipulation of process controls such as choice of catalyst, temperature, and the benzene-chlorine ratio, it is possible to maximize the production of specific chlorobenzenes; however, coproduction of higher chlorobenzenes cannot be eliminated. Further chlorination of the mono- and dichlorobenzene (DCB) forms produces higher chlorobenzenes including trichlorobenzenes, tetrachlorobenzenes, pentachlorobenzenes, and hexachlorobenzenes of which only the trichlorobenzene isomers are formed in significant amounts.

The following sections detail production processes by which monochlorobenzene, m-, o-, and p-dichlorobenzenes, isomers of trichlorobenzenes (TCBs), and hexachlorobenzene are isolated and processed. It is important to note that all processes presented are general in nature. Contact should be made with individual plants for specific processes used at their facilities. Emissions data are discussed following each process.

Process Descriptions: Monochlorobenzene

In general, the most widely used process by which benzene is chlorinated to form MCB is by passing dry chlorine into benzene gas in the presence of a catalyst in the following reaction:

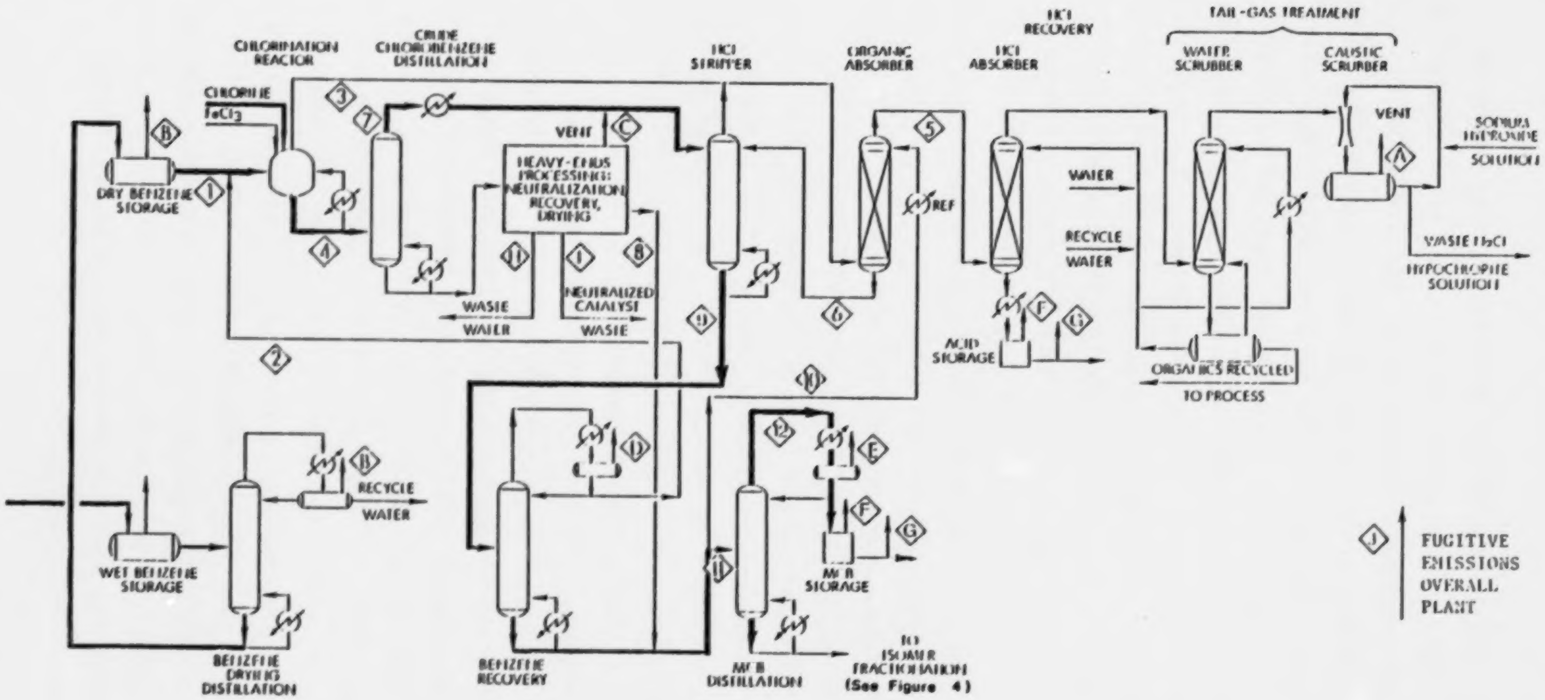


The catalyst most often used is ferric chloride; catalysts employed to a lesser extent are anhydrous aluminum chloride, stannic chloride, molybdenum chloride, Fuller's earth, and metallic iron or aluminum filings.[17] Specific processes, including the continuous, batch, and Raschig methods of benzene chlorination, are most often used in production of MCB. A purification process is then used to further separate the crude MCB from other chlorobenzene forms and impurities. Prior to the reaction for all of the above methods, benzene gas is dried either by azeotropic distillation or with silica gel, caustic soda, or alumina. Chlorine gas is prepared by scrubbing with concentrated sulfuric acid to remove moisture and impurities.[6] The chlorination then proceeds by one of the above-mentioned methods.

The continuous process is most often used because it produces high yields containing up to 95 percent MCB and small amounts of DCB isomers.

It is not possible by selecting catalyst conditions or by modifying process parameters to prevent the formation of DCBs. Basic operations that may be used in the continuous production of MCB are shown in Figure 3. The process begins with a series of small, externally cooled cast iron or steel vessels containing the catalyst (which may consist of Raschig rings of iron or iron wire). Chlorine is supplied into each vessel through suitably disposed inlets to maintain a large benzene to chlorine ratio at all points along the reaction stream. The temperature is held between 20 to 40°C to minimize the production of DCBs which form at higher temperatures. Dry benzene (Stream 1) and dried recycled benzene (Stream 2) are introduced into the reactor, which produces an overhead gas (Stream 3) and crude reaction liquid product (Stream 4). The overhead gas (Stream 3), containing HCl, unreacted chlorine, inert gases from the chlorine feed, benzene and other VOCs, is sent to an organic absorber where benzene and other VOCs are removed. The bottoms from the organic absorber (Stream 6) flow to the HCl stripper for recovery of HCl.[18] The overhead gas (Stream 5) is sent to HCl absorption. Byproduct hydrogen chloride is then removed in the HCl absorber, where it is saturated by washing with a refrigerated solvent (e.g., o-dichlorobenzene) or low vapor pressure oil, and then recovered in wash towers as commercially usable hydrochloric acid.[18,19]

Crude reaction liquid product (Stream 4) enters the crude chlorobenzene distillation column which produces overheads (Stream 7), containing most of the chlorobenzenes, unreacted benzene, and some HCl, and a bottom stream from which catalyst and other byproducts are separated (Stream 8) and processed for reuse. The overheads (Stream 7) pass through a HCl stripper and then into a benzene recovery column (Stream 9). Part of the subsequent benzene-free stream (Stream 10) is returned to the organic absorber while the remainder (Stream 11) enters the MCB distillation column. The overhead MCB distillation product (Stream 12) is then stored while the bottom stream containing DCB and TCB isomers is processed. In most cases, isomer separation processing is conducted simultaneously with MCB production but is discussed separately in subsequent sections.



NOTE: The numbers in this figure refer to process streams, as discussed in the text, and the letters designate process vents. The heavy lines represent final product streams through the process.

Figure 3. Basic operations that may be used in continuous MCB production.[18]

Under some circumstances, a batch process is used. In the batch process benzene is contained in a deep, iron or mild steel vessel lined with lead cooling coils. The catalyst, usually sublimed $FeCl_3$, is added in a benzene solution. Chlorine is fed into the bottom of the chlorinator through a lead covered pipe at a rate to maintain the temperature below 45°C in order to minimize production of DCBs.[6] The crude chlorobenzene stream and HCl waste stream are collected and treated as in the purification and recovery processes described above.

Faith, Keyes, and Clark describe a higher temperature batch process where chlorine is bubbled into a cast iron or steel tank containing dry benzene with 1 percent its own weight of iron filings.[19] Temperature is maintained at 40 to 60°C until density studies indicate that all benzene is chlorinated. The temperature is then raised to 55° to 60°C for six hours until the density rises to 1.280 g/cm^3. The same methods of chlorobenzene purification and HCl recovery in batch form are then employed. At 100 percent chlorination, the products are 80 percent monochlorobenzene, 15 percent p-dichlorobenzene, and 5 percent o-dichlorobenzene.

Another method of MCB production is the vapor phase chlorination of benzene by the Raschig process.[6] Chlorine produced by the catalytic oxidation of hydrogen chloride is introduced into a preheated mixture of benzene vapor, air and steam. The mixture is then brought into contact at 220 to 260°C with a mixed catalyst of copper oxide and oxides of Group III and VIII metals on a silica gel. To control the temperature, the catalyst is packed in small diameter tubes. To reduce DCB formation, only 10 percent of the benzene is reacted at a time. Purification and recovery proceed as indicated previously.

Emissions

The primary emissions from the production of MCB result from the tailgas treatment vent (A), where inert gases originally contained in the chlorine feed are vented (Figure 3). The vent stream also contains benzene and chlorobenzenes. Normal practice in the industry is not to provide an emission control device on this vent.[20]

Other sources of chlorobenzene emissions include: benzene drying (B), heavy-ends processing (C), benzene recovery (D), MCB distillation (E), emissions due to storage (F) and handling (G), volatilization of MCB from waste water (H), fugitive emissions during solid waste handling (I) and fugitive emissions from valves, flanges, seals, etc. (J).[20] (Note: All above letters in parenthesis refer to potential emission release points in Figure 3.)

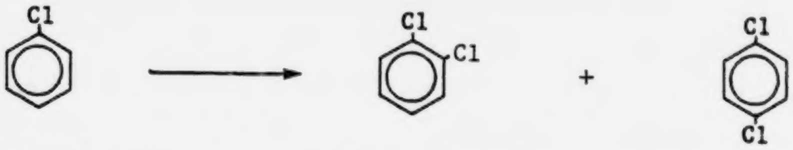
Emission factors for the production of monochlorobenzene are given in Table 3.

Source Locations

Major producers of MCB are listed in Table 4.

Process Descriptions: Dichlorobenzenes

Mixtures of dichlorobenzenes can be produced at similar or the same facilities as MCB by chlorinating MCB or benzene at 150 to 190°C in the presence of ferric chloride, as shown below.



monochlorobenzene o-dichlorobenzene p-dichlorobenzene

o- and p-Dichlorobenzene--

The residue from distillation of crude chlorobenzene, consisting mainly of o- and p-DCB, is the principal source of these isomers. Figure 4 presents basic operations that may be used to produce o- and p-DCB and TCB. In a continuation of the production of MCB, o- and p-DCB can be separated by fractional distillation. Isomer fractionation yields p-DCB (with traces of o-DCB and m-DCB) which enters the overhead (Stream 1) while the o-DCB enters the bottoms (Stream 2). The o-DCB bottoms (Stream 2) undergoes fractional distillation and produces an o-DCB overhead (Stream 3), which is sent to storage, and bottoms (Stream 4), which is further processed to yield TCBs.[18]

The crude p-DCB with other trace isomers (Stream 5) is purified by batch crystallization. Part of the purified p-DCB (Stream 6) is sent to liquid storage while the remainder (Stream 7) undergoes freezing,

TABLE 3. EMISSION FACTORS FOR A HYPOTHETICAL MONOCHLOROBENZENE PRODUCTION PLANT[21]

Emission category	kg MCB emitted per Mg MCB produced
Process	2.06
Storage	0.45
Fugitive	0.69
TOTAL	3.20

Note: The above emission factors are only general estimates derived from site visit measurements. No specific information was available on particular emission points included in each of the above emission categories or on the type of production processes used (batch or continuous) or on specific control technologies employed, if any.

Another reference estimates that total VOC emissions for a model plant (producing MCB, DCBs and TCBs by the continuous process shown in Figures 3 and 4) are 4.13 kg VOC per Mg of chlorobenzene products, of which approximately 50 percent, or 2.07 kg/Mg, is benzene.[20] From this, it can be inferred that the MCB emission factors may be considerably less than shown in the above table.

Of course, any given monochlorobenzene production plant may vary in configuration and level of control from this hypothetical facility. The reader is encouraged to contact plant personnel to confirm the existence of emitting operations and control technology at a particular facility prior to estimating emissions therefrom.

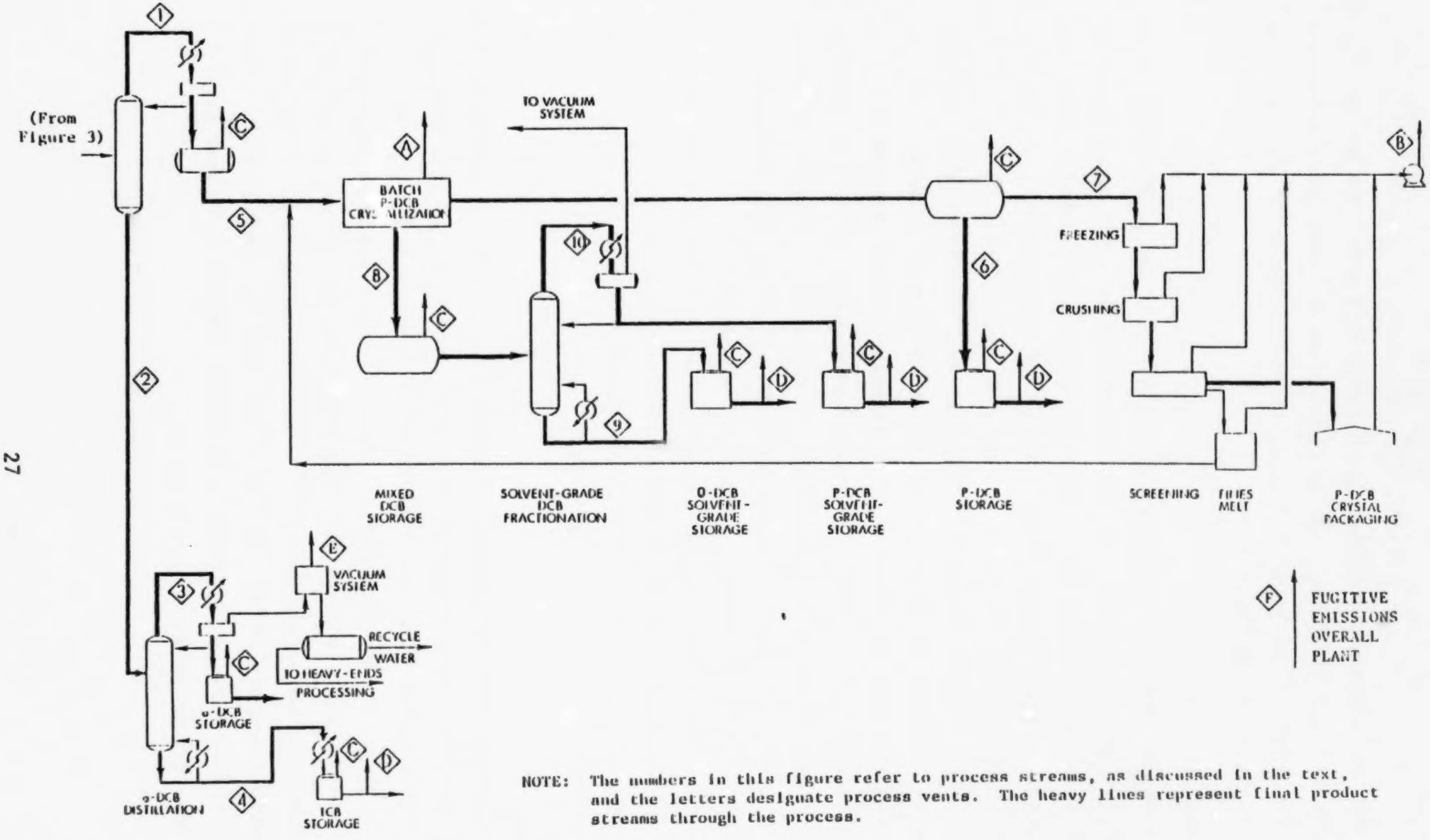
TABLE 4. CHEMICAL PRODUCERS OF MONOCHLOROBENZENE - 1984[7]

Monsanto Company
    Monsanto Industrial Chemicals Company
    Sauget, Illinois

PPG Industries, Inc.
    Chemicals Group
        Industrial Chemical Division
            Natrium, West Virginia

Standard Chlorine Chemical Company, Inc.
    Delaware City, Delaware

Note: This listing is subject to change as market conditions change, facility ownership changes, plants are closed, etc. The reader should verify the existence of particular facilities by consulting current listings and/or the plants themselves. The level of chlorobenzene emissions from any given facility is a function of variables such as capacity, throughput and control measures, and should be determined through direct contacts with plant personnel.



NOTE: The numbers in this figure refer to process streams, as discussed in the text, and the letters designate process vents. The heavy lines represent final product streams through the process.

Figure 4. Basic operations that may be used in DCB and TCB production.[18]

crushing, screening, and packaging of p-DCB crystals. The mother liquor from crystallization (Stream 8) is sent to DCB solvent grade fractionalization where it is separated into solvent grade o-DCB (Stream 9) and p-DCB (Stream 10) and stored.[18]

m-Dichlorobenzene--

Usually, m-DCB is obtained by subjecting o- and p-DCB to an isomerization process. The isomers are heated to 120°C under 650 psig pressure in the presence of aluminum chloride together with either hydrogen chloride or a small amount of water, or alternatively at a higher temperature in the presence of aluminum chloride alone.[17] As an option, higher chlorinated benzenes can be reduced with hydrogen at 350 to 500°C in the presence of cuprous halide on alumina. TCB mixtures have also been reduced with hydrogen in the presence of catalysts such as molybdenum oxide, chromium oxide, or nickel chloride.[6] Also, 100 percent m-DCB can be formed by catalytically reducing 1,3,5-TCB for 7 hours at 205°C. Excess hydrogen and by-product hydrogen chloride are removed through a reflux condenser.[1]

Crowder and Gilbert (1958) patented a vapor-phase dehalogenation of 1,3,5-TCB using platinum on activated charcoal as a catalyst at 375°C and 1 psig pressure. Distillation of products by this method yields 65 percent m-DCB.[1]

Emissions

Emissions from the continuous process (Figure 4) are primarily from the batch p-DCB crystallization vent (A). An exhaust fan (B) releases sublimation losses from freezing, crushing, and the p-DCB crystal packaging hoods to the atmosphere. Some emissions are also expected from liquid product storage (C), handling (D), and the vacuum system (E) which services the vacuum stills.[20] Fugitive emissions may be expected from certain valves, pumps, etc. (F). Data are not available to estimate emissions from the production of m-DCB. Emission factors for o- and p-DCBs are shown in Tables 5 and 6.

TABLE 5. EMISSION FACTORS FOR A HYPOTHETICAL O-DICHLOROBENZENE PRODUCTION PLANT[22]

Emission category	kg o-DCB emitted per Mg o-DCB produced
Process	2.32
Storage	0.47
Fugitive	0.76
TOTAL	3.55

Note: The above emission factors are only general estimates derived from site visit measurements. No specific information was available on particular emission points included in each of the above emission categories or on the type of production processes used (batch or continuous) or on specific control technologies employed, if any.

Another reference estimates that total VOC emissions for a model plant (producing MCB, DCBs and TCBs by the continuous process shown in Figures 3 and 4) are 4.13 kg VOC per Mg of chlorobenzene products, of which approximately 50 percent, or 2.07 kg/Mg, is benzene.[20] From this, it can be inferred that the o-DCB emission factors may be considerably less than shown in the above table.

Of course, any given o-dichlorobenzene production plant may vary in configuration and level of control from this hypothetical facility. The reader is encouraged to contact plant personnel to confirm the existence of emitting operations and control technology at a particular facility prior to estimating emissions therefrom.

TABLE 6. EMISSION FACTORS FOR A HYPOTHETICAL P-DICHLOROBENZENE PRODUCTION PLANT[22]

Emission category	kg p-DCB emitted per Mg p-DCB produced
Process	5.81
Storage	0.41
Fugitive	1.02
TOTAL	7.24

Note: The above emission factors are only general estimates derived from site visit measurements. No specific information was available on particular emission points included in each of the above emission categories or on the type of production processes used (batch or continuous) or on specific control technologies employed, if any.

Another reference estimates that total VOC emissions for a model plant (producing MCB, DCBs, and TCBs by the continuous process shown in Figures 3 and 4) are 4.13 kg VOC per Mg of chlorobenzene products, of which approximately 50 percent, or 2.07 kg/Mg, is benzene.[20] From this, it can be inferred that the p-DCB emission factors may be considerably less than shown in the above table.

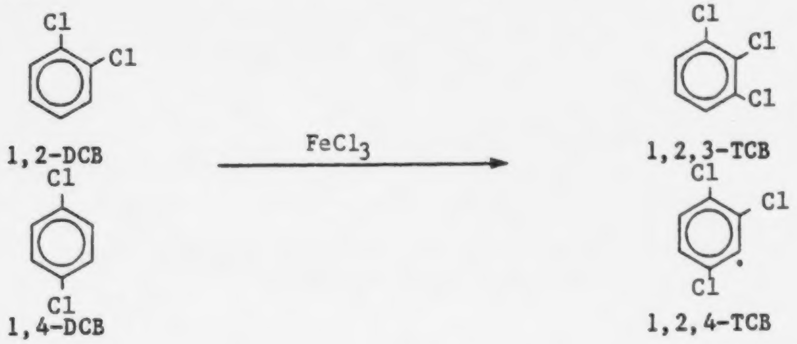
Of course, any given p-dichlorobenzene production plant may vary in configuration and level of control from this hypothetical facility. The reader is encouraged to contact plant personnel to confirm the existence of emitting operations and control technology at a particular facility prior to estimating emissions therefrom.

Source Locations

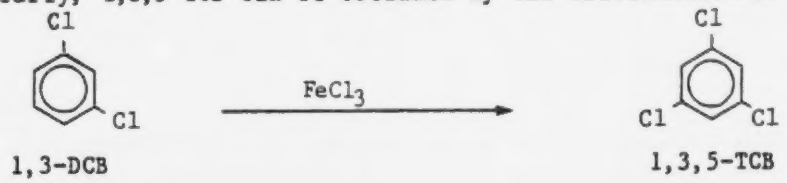
Major producers and processors of o- and p-DCB are listed in Table 7. No information concerning producers of m-DCB is available.

Process Descriptions: Trichlorobenzenes

The most common process by which trichlorobenzenes are formed is the catalytic chlorination of o- and p-DCB at 20 to 30°C in the presence of ferric chloride. The reaction is allowed to proceed until a density of 1.4 at 15°C is obtained, at which time the acid is neutralized and the products are fractionally distilled to yield 1,2,4- and 1,2,3-isomers.[1]



Similarly, 1,3,5-TCB can be obtained by the chlorination of m-DCB.



Most TCBs are produced at the same location as the lower chlorinated benzenes where the TCBs are fractionally separated from DCBs.[6] It is assumed that most TCBs are produced by the batch method due to the low volume of domestic production.[1]

Other trichlorobenzene production processes mentioned in the literature include: (1) the reaction of α, β, or γ-benzene hexachloride with alcoholic potash at 100°C to produce all three TCB isomers; (2) the dehalogenation of α-benzene hexachloride with pyridine to form all three TCB isomers; and (3) the reaction of α-benzene hexachloride with calcium hydroxide to form primarily 1,2,4-TCB.[6] Further

TABLE 7. CHEMICAL PRODUCERS OF O-DICHLOROBENZENE AND P-DICHLOROBENZENE - 1984[8,9]

Monsanto Company
    Monsanto Industrial Chemicals Company
    Sauget, Illinois

PPG Industries, Inc.
    Chemicals Group
        Industrial Chemical Division
            Natrium, West Virginia

Specialty Organics Inc.
    Irwindale, California   processor - (see note)

Standard Chlorine Chemical Company, Inc.
    Delaware City, Delaware

Note: Producers manufacture a variety of chlorinated benzenes; processors purchase a mixture of chlorobenzenes and isolate specific dichlorobenzene isomers. This listing is subject to change as market conditions change, facility ownership changes, plants are closed, etc. The reader should verify the existence of particular facilities by consulting current listings and/or the plants themselves. The level of chlorobenzene emissions from any given facility is a function of variables such as capacity, throughput and control measures, and should be determined through direct contacts with plant personnel.

process details are not available. Contact should be made with specific plants to determine manufacturing processes used on site.

Emissions

Trichlorobenzene emissions released during the continuous product process (Figure 4) result from storage (C) and handling (D) of trichlorobenzene products. Fugitive emissions of TCBs may also occur when leaks develop in valves, pump seals, and major equipment (F). Secondary emissions from MCB production (Figure 3) are also possible from volatilization of TCB from waste water stream (H) containing dissolved benzene and other VOCs, and the catalyst waste stream (I).[20] No information was available concerning identification of specific TCB isomers.

Source Locations

Table 8 summarizes the locations of plants which manufacture specific isomers of TCB.

Process Description: Hexachlorobenzene

Although hexachlorobenzene production has been discontinued in the United States, literature cites two basic direct synthesis methods available for HCB production which are: (1) the reaction of hexachlorocyclohexane isomers with sulfuryl chloride or chlorosulfonic acid and (2) the reaction of benzene with chlorine in the presence of ferric chloride.[24]

HCB is produced by refluxing hexachlorocyclohexane ($C_6H_6Cl_6$) isomers with sulfuryl chloride (SO_2Cl_2) or chlorosulfonic acid ($HClSO_3$) in the presence of a ferric chloride or aluminum chloride catalyst (Figure 5). After refluxing for several hours at 130 to 200°C, the product stream is cooled to promote crystallization. HCB crystals are then separated by filtration or centrifugation and then washed and dried for packaging.[24]

HCB is also produced by reacting benzene with excess chlorine in the presence of ferric chloride at 150 to 200°C (Figure 6). The product stream is scrubbed to remove hydrogen chloride. Gaseous chlorobenzenes in the stream are returned to the reactor, while the remaining reaction products are cooled to less than 100°C to crystallize HCB. The HCB is then separated by centrifugation, washed, dried, and packaged.[24]

TABLE 8. CHEMICAL PRODUCERS OF TRICHLOROBENZENE - 1984[23]

1,2,3-Trichlorobenzene

Standard Chlorine Chemical Company, Inc.
Delaware City, Delaware

1,2,4-Trichlorobenzene

Standard Chlorine Chemical Company, Inc.
Delaware City, Delaware

1,3,5-Trichlorobenzene

Southland Corporation
Chemical Division
Great Meadows, New Jersey

Mixed Isomers

PPG Industries, Inc.
Chemicals Group
Industrial Chemical Division
Natrium, West Virginia

Note: This listing is subject to change as market conditions change, facility ownership changes, plants are closed, etc. The reader should verify the existence of particular facilities by consulting current listings and/or the plants themselves. The level of chlorobenzene emissions from any given facility is a function of variables such as capacity, throughput and control measures, and should be determined through direct contacts with plant personnel.

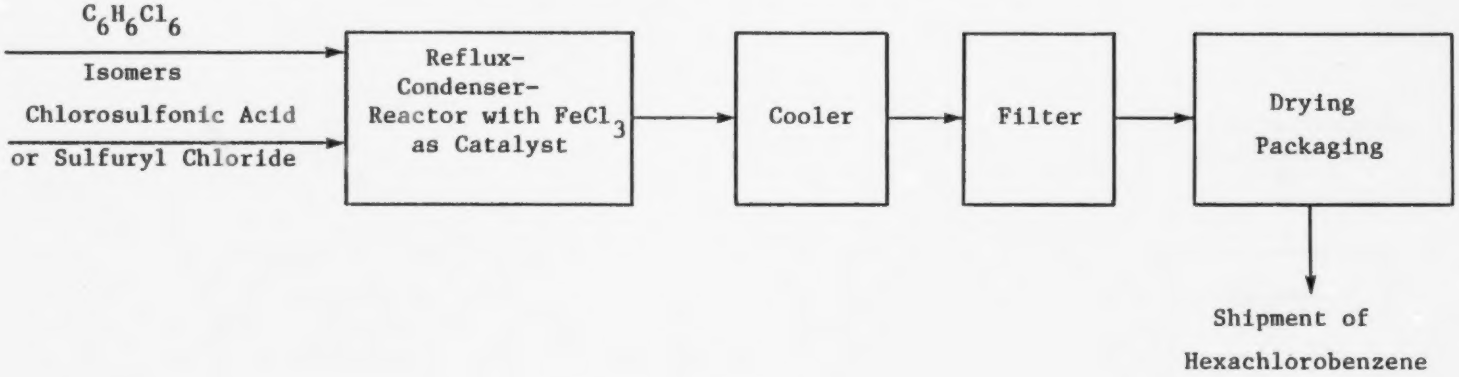


Figure 5. Production schematic for hexachlorobenzene from hexachlorocyclohexane.[24]

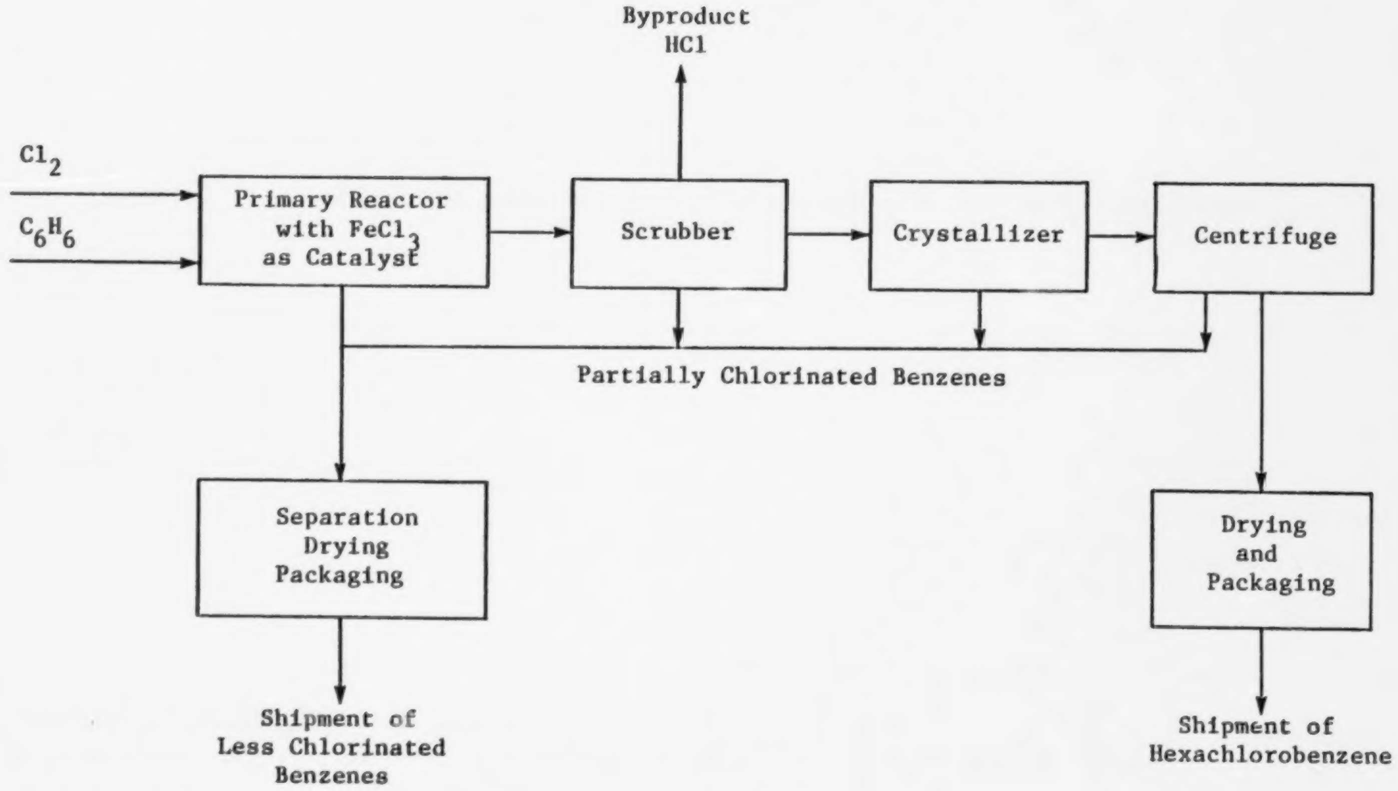

Byproduct HCl
Cl_2
C_6H_6
Primary Reactor with $FeCl_3$ as Catalyst
Scrubber
Crystallizer
Centrifuge
Partially Chlorinated Benzenes
Separation Drying Packaging
Drying and Packaging
Shipment of Less Chlorinated Benzenes
Shipment of Hexachlorobenzene

Figure 6. Production schematic for hexachlorobenzene by chlorination of benzene.[24]

No information was found in the literature to suggest that either of these reactions has been used commercially to produce HCB. The most common method of HCB generation is by recovering it from the waste byproduct streams in chlorinated solvents production.[24] Recovery of HCB as a byproduct of chlorinated solvent production is discussed in the section entitled "HCB Generation during Chlorinated Solvent Production."

Emissions

No information is available concerning emissions from either method of direct production of HCB.

Source Locations

Commercial production of HCB in the United States was discontinued around 1975. In the literature, three companies at three locations were identified to be producing HCB at some time as a product chemical. These companies were Dover Chemical, Dover, Ohio; Hummel Chemical, South Plainfield, New Jersey; and Stauffer Chemical, Louisville, Kentucky. Reportedly, Hummel Chemical only repackaged and distributed HCB produced by Dover Chemical. Regardless of the exact number of producers, it is known that all companies manufactured HCB by recovering it from waste byproduct streams generated by chlorinated solvents production.[24]

According to information received from HCB users, there is little HCB still produced worldwide. One HCB fungicide manufacturer in Canada reported that he had only been able to locate one supplier of HCB anywhere and this was located in Spain.[24]

USE OF CHLOROBENZENES IN THE PRODUCTION OF DYES AND PIGMENTS

The uses of chlorobenzenes in the dye and pigment industry are twofold: (1) to synthesize other intermediates which are subsequently utilized in the formation of specific dyes and pigments; and (2) as inert process solvents in dye and pigment manufacturing. The following describes the use of chlorobenzenes in each of the above applications. The Ecological and Toxicological Associates of the Dyestuffs Manufacturing Industry indicates that the process information mentioned below is outdated; however no new information was provided.[25]

Use of Chlorobenzenes in the Synthesis of Intermediates

The chlorobenzene group is one of many classes of compounds used to synthesize intermediates in the dye and pigment industry. Chlorobenzenes are normally purchased outside of the industry, converted into more complex intermediates and ultimately into dyes and pigments. Some of the intermediates may be dyes themselves so that the distinction between them and dyes and pigments is somewhat arbitrary. Figures 7 through 10 show the various reactions involving chlorobenzenes.

Process Description--

In the dye and pigment industry, reactions for the production of intermediate dyes are generally carried out in kettles made from cast iron, stainless steel, or steel lined with rubber, glass (enamel), brick, or carbon blocks. The kettles have capacities of 500 to 10,000 gallons and are equipped with mechanical agitators, thermometers or temperature recorders, condensers, pH probes, etc., depending on the nature of operation. Jackets or coils serve to heat by circulation of high-boiling fluids (hot oil, Dowtherm®), steam or hot water. The kettles may be cooled with chilled brine. Unjacketed kettles are often used for aqueous reactions where heating is effected by direct introduction of steam and cooling is effected by addition of ice or by the use of heat exchangers.[27]

Products are transferred from one piece of equipment to another by gravity flow, pumping, or by blowing with air or inert gas. Solids are separated by either centrifuges, filter boxes, continuous belt filters, and either plate-and-frame or recessed plate filter presses.

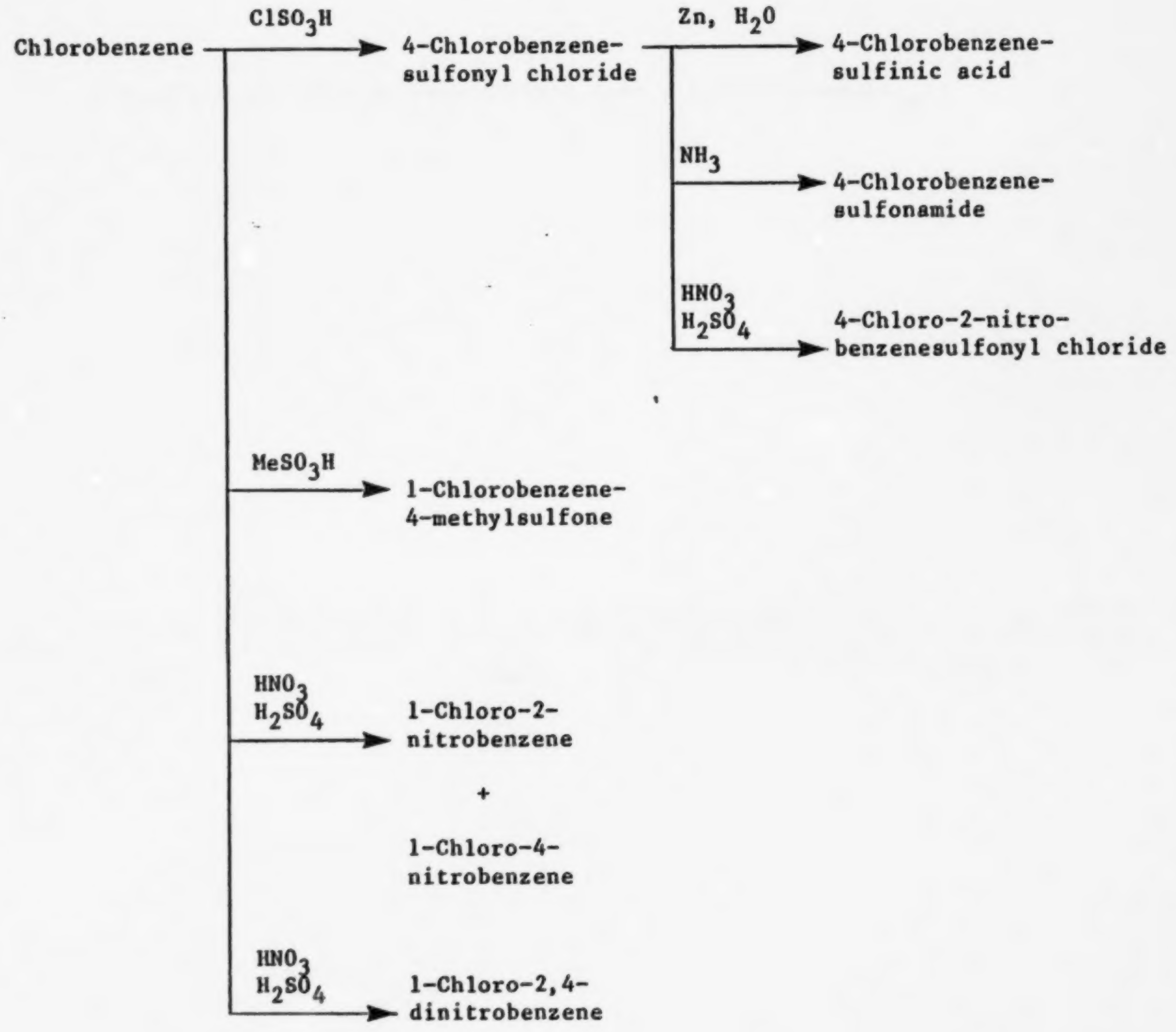

Chlorobenzene
$ClSO_3H$
4-Chlorobenzene-sulfonyl chloride
Zn, H_2O
4-Chlorobenzene-sulfinic acid
NH_3
4-Chlorobenzene-sulfonamide
HNO_3 H_2SO_4
4-Chloro-2-nitro-benzenesulfonyl chloride
$MeSO_3H$
1-Chlorobenzene-4-methylsulfone
HNO_3 H_2SO_4
1-Chloro-2-nitrobenzene
+
1-Chloro-4-nitrobenzene
HNO_3 H_2SO_4
1-Chloro-2,4-dinitrobenzene

Figure 7. Dye intermediates derived from monochlorobenzene.[26]

$$\text{o-Dichlorobenzene} \xrightarrow{\text{Oleum}} \text{3,4-Dichlorobenzenesulfonic acid} \xrightarrow{HNO_3} \text{4,5-Dichloro-2-nitrobenzenesulfonic acid} \xrightarrow{\text{Red'n}} \text{2-Amino-4-5-dichlorobenzenesulfonic acid}$$

Figure 8. Dye intermediate derived from o-dichlorobenzene[26]

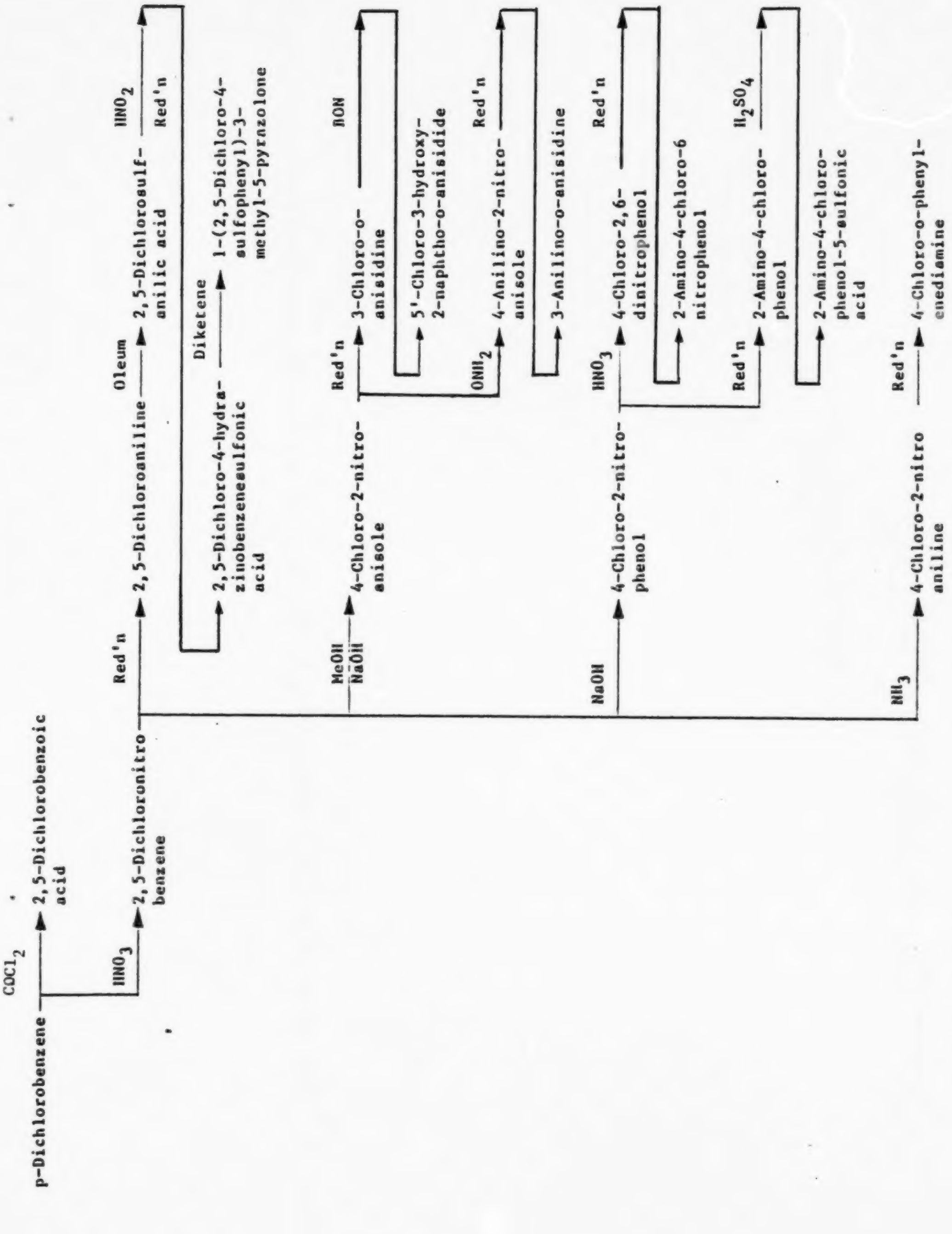


Figure 9. Dye intermediates derived from p-dichlorobenzene.[26]

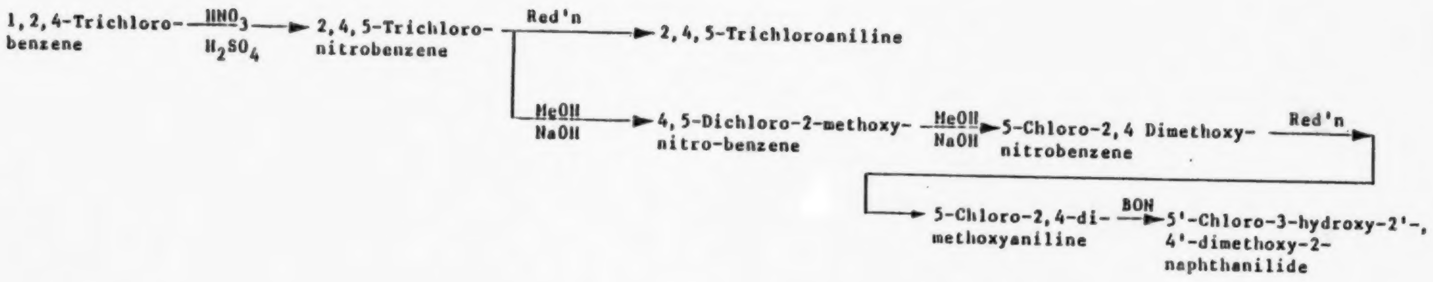

1,2,4-Trichloro-benzene
HNO3
H2SO4
2,4,5-Trichloro-nitrobenzene
Red'n
2,4,5-Trichloroaniline
MeOH
NaOH
4,5-Dichloro-2-methoxy-nitro-benzene
MeOH
NaOH
5-Chloro-2,4 Dimethoxy-nitrobenzene
Red'n
5-Chloro-2,4-di-methoxyaniline
BON
5'-Chloro-3-hydroxy-2'-, 4'-dimethoxy-2-naphthanilide

Figure 10. Synthesis of various intermediates for dye and pigment production from 1,2,4-trichlorobenzene.[26]

When possible, intermediates are taken for subsequent manufacture without drying. When drying is required, air or vacuum ovens, rotary dryers, or spray dryers are used. Drum dryers (flakers) may also be used, although less commonly. Dyestuffs which require wet grinding, especially disperse dyes, are often spray dried with solid diluents to achieve standardization.

Small tonnages of numerous intermediates needed exclusively by the dye industry have made continuous processes impractical. Batch processes remain the rule but progress in computer and electronic technologies has led to a growing use of automatic process control.[27]

Use of Chlorobenzenes as Process Solvents

Chlorobenzenes find uses as inert process solvents in the production of a number of dyes and pigments. In Table 9, dyes and pigments which use specific chlorinated benzenes as solvents are categorized into dye or pigment classes according to the nature of their chemical structure. Individual dyes and pigments within a class are produced by the same processes as described below.

Description of Process Using MCB--

MCB is used as a process solvent in the manufacture of seven indigoid dyes and pigments. Of these, six are thioindigoid colors and one is a hybrid of indigo (C.I. 73000) and a specially made intermediate structurally related to the thioindigo colors. Due to the corrosive nature of the reactants involved in these processes, glass-lined vessels and efficient stirring are required.[28]

The manufacture of the thioindigoid colors involves two process steps, one of which is a diazotization. Because low temperatures are required, ice is used in substantial quantities. Temperature conditions range from 0 to 70°C.[28] Information regarding these processes is somewhat limited.

In the production of the hybrid dye, one of the reaction steps is exothermic and must be maintained below 17°C to obtain a high yield. Another reaction requires a temperature of 125°C, using MCB as the process solvent.[28]

TABLE 9. DYES AND PIGMENTS UTILIZING CHLOROBENZENE SOLVENTS

Chlorobenzene Solvent	Dye or Pigment Class	Color Index (C.I.)	Dye or Pigment Name
Monochlorobenzene	Thioindigoid	73310	Pigment Red 87
	Thioindigoid	73312	Pigment Red 88
	Thioindigoid	73335	Vat Orange 5
	Thioindigoid	73360	Vat Red 1, Pigment Red 181, D+C Red 30,
	Thioindigoid	73385	Vat Violet 2 Pigment Violet 36
	Thioindigoid	73390	Pigment Red 198
	Indigoid	73670	Vat Black 1
o-Dichlorobenzene	Xanthene	45180	Mordant Red 27
	Oxazine	51300	Direct Blue 106
	Oxazine	51319	Pigment Violet 23
	Pyranthrone	59700	Vat Orange 9
	Anthraquinone	61725	Vat Yellow 3
	Anthraquinone	63365	Vat Violet 17
	Anthraquinone	65049	Pigment Yellow 123
	Anthraquinone	68420	Pigment Yellow 108
	Anthraquinone (oxazole)	67000	Vat Red 10
1,2,4-Trichlorobenzene	Benzanthrone	59825	Vat Green 1
	Antraquinone	61725	Vat Yellow 3
	Anthraquinone	63365	Vat Violet 17
	Anthraquinone	65049	Pigment Yellow 123
	Anthraquinone	68420	Pigment Yellow 108

Description of Process Using o-DCB--

o-DCB is used as a process solvent in the production of one xanthene dye, one oxazine dye, one oxazine pigment, one pyranthrone dye, and five anthraquinone dyes. In addition, these dyes may be used to produce other related dyes and pigments by halogenation.

As many as three process steps may be required in the production of xanthene dyes.[29] The required reactions are carried out in glass-lined batch reactor vessels with continuous stirring under atmospheric pressure. o-DCB is used as a process solvent to make the xanthene dye with a color index of 45180 (Mordant Red 27). The initial condensation reaction is carried out with a 100 percent stoichiometric excess of sulfuric acid which is later recovered.

The initial condensation reaction in zanthene dye production is carried out with 5-hydroxytrimellitic acid and a 100 percent stiochiometric excess of sulfuric acid which is later recovered. m-Diethylaminophenol is added gradually to the other reactants over a period of 3 hours at 150 to 180°C. Cyclization of the intermediate product is accomplished with 78 percent sulfuric acid at 175 to 180°C for 3 hours.

The manufacture of oxazine dyes and pigments involves the condensation of a substituted aniline compound with a substituted phenolic compound (or a phenol ether), followed by an oxidative reaction which forms the oxazine ring system.[30] Stirred batch reactors with glass linings are required for most of the reactions involved in making these products. The oxazine pigment (C.I. 51319) is produced by condensing chloranil with 3-amino-9-ethylcarbazole using sodium acetate as catalyst. o-DCB is used as the process solvent in the reaction which requires 7 hours at 60 to 115°C. The condensation product is cyclized (refers to ring formation) to the pigment with benzenesulfonyl chloride at 180°C. The crude pigment is subsequently washed and filtered. o-DCB is also used as a process solvent in the manufacture of an oxazine pigment (C.I. 51300); however, no specific process information was available.

Pyranthrone (C.I. 59700) can be made from either 1-chloro-2-methylanthraquinone or pyrene as the principal organic starting material.[31] Glass-lined, stirred reaction vessels are required due to the corrosive nature of the reactants. o-DCB is used as a process solvent in this process. The dimerization of the 1-chloro-2-methyl-anthraquinone takes place at 150 to 160°C in 6 hours while cyclization to the dye requires a further 3 hours at the same temperature.

Of the five anthraquinone dyes which use o-DCB as a process solvent, four are amides of aminoanthraquinone compounds.[32] The amides are made by the reaction of an aromatic carboxylic acid chloride with the selected amino compound at temperatures between 50 and 160°C. Glass-lined reactor vessels are required along with good stirring. Cooling of the exothermic reacting mixture may be necessary as the starting materials are combined. An inert organic solvent is required for this process which dissolves the starting materials well and has a high boiling point. o-DCB and TCB are typically used here.

The other anthraquinone dye which uses o-DCB as a process solvent is an oxazole compound (with C.I. 67000) and is made from 2-amino-3-hydroxy anthraquinone.[33] Batch type reaction vessels made of iron and with good stirrers are typically used. In addition, the reactor must have a cooling coil to remove heat generated by the moderately exothermic first reaction between the aminoanthraquinone and the acid chloride. The cyclization of the resulting amide to the desired oxazole is carried out in o-DCB at 140°C in 5 hours.

Description of Process Using TCB--

TCB is used as a process solvent in the halogenation of dyes and in the production of benzanthrone dyes.[34] The halogenated product is obtained by treating the simple dye itself with a halogen or a halogen carrying compound. These reactions can usually be carried out in iron equipment provided that moisture is rigorously excluded; however, glass-lined equipment is often used. Water scrubbers are generally used to trap the effluent hydrogen halide which is formed in most cases. Of the halogen used, only half appears in the product with the remainder being converted to the hydrogen halide. A compound which typically functions as a halogen source is sulfuryl chloride. When this compound is used, both sulfur dioxide and hydrogen chloride are by-products. Halogenations are generally carried out at temperatures in the range of 40 to 55°C although some cases require temperatures as high as 155 to 190°C.

TCB is known to be used as a process solvent in the production of a benzanthrone dye commonly called Vat Green 1 (C.I. 59825).[35] Iron vessels with good stirring may be used. The manufacture of benzanthrone dyes depends on the modification of the primary intermediate, benzanthrone. In order to make Vat Green 1, three process steps are required. The alkali treatment of benzanthrone to make dibenzanthronyl takes place at 112°C for 1 to 4 hours. The dibenzanthronyl is then oxidized to the diketo compound at 25 to 30°C for 4 hours. The methylation of the dihydroxy compound is achieved by reducing the diketo compound with boiling sodium bisulfite at 210°C for 4 hours.

As noted in the discussion on the amide production of anthraquinone dyes, TCB is often used as a process solvent.

Emissions

Emission factors for the use of o-DCB in dye synthesis appear in Table 10. Literature information does not distinguish between emissions resulting from the synthesis of intermediates or process solvent usage. Information regarding the nature and quantities of air emissions of other chlorobenzenes produced during dye and pigment manufacture was not available. The reader is advised to seek emissions data through contact with specific plant personnel.

Source Locations

A list of dye and pigment manufacturers which may utilize chlorobenzenes in certain processes is contained in Table 11. The Ecological and Toxicological Association of Dyestuffs Manufacturing Industry indicates that this list is outdated and does not reflect the major restructuring which has occurred in the industry during recent years.[25] No new information was provided, however. Ciba Geigy of Greensboro, North Carolina, reports to have used chlorobenzenes as process solvents but has discontinued the production of vat dyes (anthraquinone type) which utilized them.[37]

TABLE 10. EMISSION FACTORS FOR O-DICHLOROBENZENE IN DYE SYNTHESIS[22]

Emission category	kg o-DCB emitted per Mg dye produced
Process	0.40
Storage	0.05
Fugitive	0.05
TOTAL	0.50

Note: These emission factors are only general estimates. No information is available on specific emission points included in each emission category, the type of production processes used, or specific control technologies employed, if any. Any given dye synthesis plant may vary in configuration and level of control from this hypothetical facility. The reader is encouraged to contact plant personnel to confirm the existence of emitting operations and control technology at a particular facility prior to estimating emissions therefrom.

TABLE 11. DYE AND PIGMENT MANUFACTURING COMPANIES - 1984[36]

New Jersey

1. American Cyanamid Company
Organic Chemicals Division
Wayne, New Jersey

2. Atlantic Industries
Nutley, New Jersey

3. BASF Wyandotte Corporation
Paper Colors and Chemicals Department
Parsippany, New Jersey
Pigments Division
Parsippany, New Jersey

4. Buffalo Color Corporation
West Paterson, New Jersey

5. Color-Chem International Corporation
Glen Rock, New Jersey

6. Chem-Mark, Inc.
Bound Brook, New Jersey

7. Dye Specialties Inc.
Secaucus, New Jersey

8. Fabricolor Inc.
Paterson, New Jersey

9. Heubach Inc.
Newark, New Jersey

10. Indol Color Company, Inc.
Elizabeth, New Jersey

11. International Dyestuffs Corporation
Clifton, New Jersey

12. Leeben Color
Division of Tricon Colors, Inc.
Elmwood Park, New Jersey

(continued)

TABLE 11. (continued)

New Jersey (continued)

13. Mobay Chemical Corporation
    Dyes and Pigments Division
    Union, New Jersey
    Dyes and Pigments Division
    Pigments Department
    Hawthorne, New Jersey

14. Passaic Color and Chemical Company
    Paterson, New Jersey

15. Pfister Chemical Inc.
    Ridgefield, New Jersey

16. Pope Chemical Corporation
    Paterson, New Jersey

North Carolina - South Carolina

1. American Hoechst Corporation
   Specialty Products Group
   Dyes and Textile Chemicals Department
   Charlotte, North Carolina

2. BASF Wyandotte Corporation
   Colors and Auxilaries Division
   Charlotte, North Carolina

3. Carolina Color & Chemical Corporation
   Charlotte, North Carolina

4. Ciba-Geigy Corporation
   Greensboro, North Carolina

5. Crompton & Knowles Corporation
   Charlotte, North Carolina

6. Crown Metro Inc.
   Greenville, South Carolina

7. C.H. Patrick & Company, Inc.
   Greenville, South Carolina

(continued)

TABLE 11. (continued)

North Carolina - South Carolina (continued)

8. Sandoz Colors and Chemicals
   Charlotte, North Carolina

9. Sodyeco Inc.
   Charlotte, North Carolina

10. Synalloy Corporation
    Blackman Uhler Chemical Division
    Spartanburg, South Carolina

Ohio

1. Day-Glo Color Corporation
   Cleveland, Ohio

2. Sterling Drug Inc.
   Hilton-Davis Chemical Group
   Cincinnati, Ohio

3. Sun Chemical Corporation
   Cincinnati, Ohio

New York

1. Bern Colors - Poughkeepsie Inc.
   Poughkeepsie, New York

2. Chemische Fabric Rohner AG
   Hauppauge, New York

3. Pylam Products Company, Inc.
   Garden City, New York

Pennsylvania

1. Allegheny Chemical Corporation
   Ridgeway, Pennsylvania

2. John Campbell & Company, Inc.
   Perkasie, Pennsylvania

(continued)

TABLE 11. (continued)

Pennsylvania (continued)

3. C. Lever Company, Inc.
   Bensalem, Pennsylvania

Miscellaneous

1. Carroll Products Inc.
   Wood River Junction, Rhode Island

2. Carey Industries Inc.
   Danbury, Connecticut

3. Eastman Chemical Product, Inc.
   Kingsport, Tennessee

4. GCA Corporation
   Stamford, Connecticut

5. ICI Americas Inc.
   Wilmington, Delaware

6. Morton Thiokol, Inc.
   Morton Chemical Division
   Chicago, Illinois

7. Organic Chemical Corporation
   East Providence, Rhode Island

8. Warner-Jenkinson Company
   St. Louis, Missouri

Note: This listing is subject to change as market conditions change, facility ownership changes, plants are closed, etc. The reader should verify the existence of particular facilities by consulting current listings and/or the plants themselves. The level of chlorobenzene emissions from any given facility is a function of variables such as capacity, throughput and control measures, and should be determined through direct contacts with plant personnel.

USE OF CHLOROBENZENES AS SOLVENTS IN ORGANIC SOLVENT CLEANING OPERATIONS

Chlorobenzenes are employed as cleaning and degreasing agents in solvent cleaning operations to remove water-insoluble soils from metal, plastic, fiberglass or other surfaces. o-DCB is contained in automobile cleaners; carburetor cleaners; in formulations to remove paints, inks, varnishes, lacquers, resins, gums, waxes, heavy greases, acetylcellulose, sulfur and organic sulfur compounds, and tarry substances in stills and processing equipment; shoe polish; metal polish; rust preventatives; and other cleaning/polishing formulations.[38] 1,2,4-TCB is used in degreasing formulations for electronic wafer stripping in the electronic components industry and engine cleaning.[39]

Many cleaning processes are performed in organic solvent cleaners using solvent formulations which include chlorobenzenes. Table 12 compares properties of known solvents used in degreasing with properties of chlorobenzenes. Organic solvent cleaning (degreasing) is used in manufacturing processes in preparation for painting, plating, inspection, repair, assembly, heat treatment or machining. Types of organic solvent cleaners which may utilize chlorobenzenes include cold cleaners and conveyorized degreasers.

The simplest and least expensive organic solvent cleaners are cold cleaners which use solvents at room temperature. A cold cleaner usually consists of a tank containing non-boiling solvent and a draining surface or basket. Typical operations are spraying, flushing and immersion using room temperature or slightly heated solvent solution made up of a petroleum-derived solvent, halogenated solvent or a solvent blend.[41] A blended solvent used in carburetor and automobile parts marketed by Safety-Kleen Corporation contains methylene chloride, o-DCB, and cresylic acid, covered by an aqueous soap solution.[40] Two basic cold cleaner designs are the conventional cold cleaner (dipping tank) shown in Figure 11 and the remote reservoir cold cleaner. In the remote reservoir cold cleaner, parts are sprayed in a work space which drains to an enclosed reservoir, preventing evaporative loss. Agitation by means of pumping, compressed air, vertical agitation or ultrasound increases cleaning efficiencies of dip tanks.[41]

TABLE 12. PROPERTIES OF HALOGENATED SOLVENTS USED IN ORGANIC SOLVENT CLEANERS[40]

Solvents	Boiling point (°C)	Vapor pressure (mmHg @ 25°C)	Vapor density (Air = 1.0)	Molecular weight	Weight density (kg/l)	Water solubility (g/100g)
Most widely used						
Trichloroethylene	86.7	75.0	4.5	131.40	1.45	0.107 (20°C)
Perchloroethylene	120.8	18.6	5.7	165.85	1.61	0.015 (25°C)
1,1,1-Trichloroethane	74.1	123.0	4.6	133.42	1.31	0.095 (20°C)
Methylene Chloride	39.8	438.0	2.9	84.94	1.32	1.32 (20°C)
Trichlorotrifluoroethane	47.6	796.0	6.5	187.0	1.58	0.017 (25°C)
Chlorobenzenes*						
o-Dichlorobenzene	180.5	1.45	5.1	147.0	1.31	1.45 (20°C)
1,2,4-Trichlorobenzene	213.0	0.29	---	181.5	1.46	insol.
1,3,5-Trichlorobenzene	208.0	0.15	---	181.5	---	insol.
1,2,3-Trichlorobenzene	218.0	0.07	---	181.5	---	insol.

*Note: MCB is not used as a cleaning solvent.

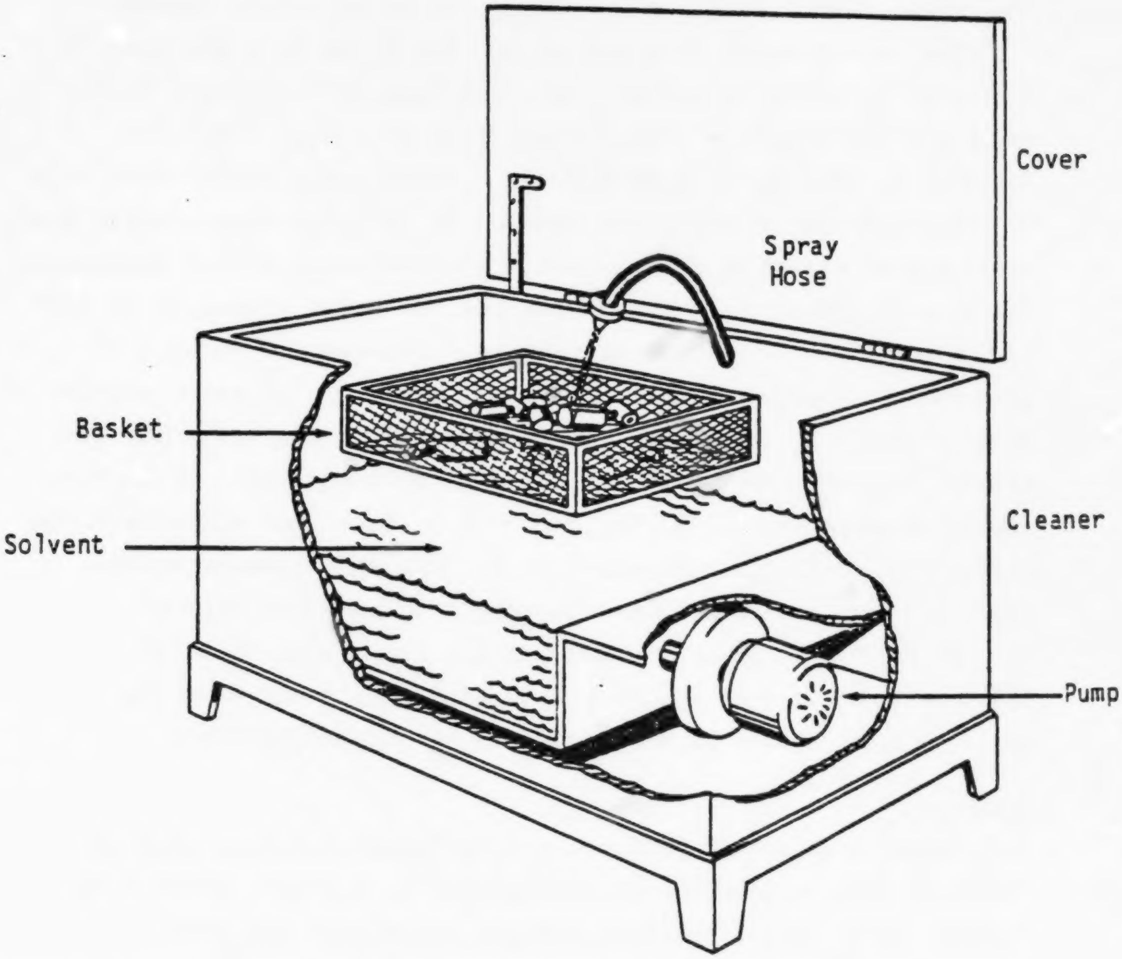


Figure 11. Cold cleaner.[41]

Conveyorized degreasers are continuous or batch loading units which employ a cold cleaner. The units are enclosed to prevent solvent losses due to air movement in the plant. Seven types include monorail, cross-rod, vibra, ferris wheel, belt, strip, and circuit board cleaners.[41]

The circuit board degreaser is similar to the belt degreaser shown in Figure 12, which is designed to clean long and thin parts.[41] The three types of cleaners used in production of circuit boards are developers, strippers and defluxers. In the process, ultraviolet light in the pattern of an electrical circuit is projected onto a copper sheet covered with resist (a photosensitive material with special properties). The image of the circuit pattern exposes the resist causing it to bond to the surface of the metal. A developer degreaser is employed to dissolve the unexposed resist; unexposed copper is removed by etching in an acid bath. At this time, the stripper (containing 1,2,4-TCB) dissolves the developed resist and a wave of solder passes over the bare circuit bonding to it. The defluxer removes flux left after the solder hardens. Depending on the nature of the materials cleaned, circuit board cleaners use either room temperature solvents or vapors.

No further information exists on the actual quantities of chlorobenzenes used or specific processes or equipment which are employed for the uses of chlorobenzenes as cleaning solvents.

Emissions

Types of emissions produced by cold cleaning include those generated by bath evaporation to surrounding air, solvent carry-out of cleaned parts, agitation, waste solvent evaporation and spray evaporation.[42] Emissions associated with conveyorized degreasers result from the same processes but to a lesser degree because of the nearly complete enclosure of the conveyorized system. Some emissions are also expected from evaporation of blended cleaning solvents during mixing and handling.[42]

Uncontrolled emissions from degreasers can be approximated by material balance by assuming that the quantity of makeup solvent is equal to the amount of solvent evaporated from the process, over the long term. To estimate emissions after controls by material balance, the quantity of solvent collected or destroyed in control devices, and

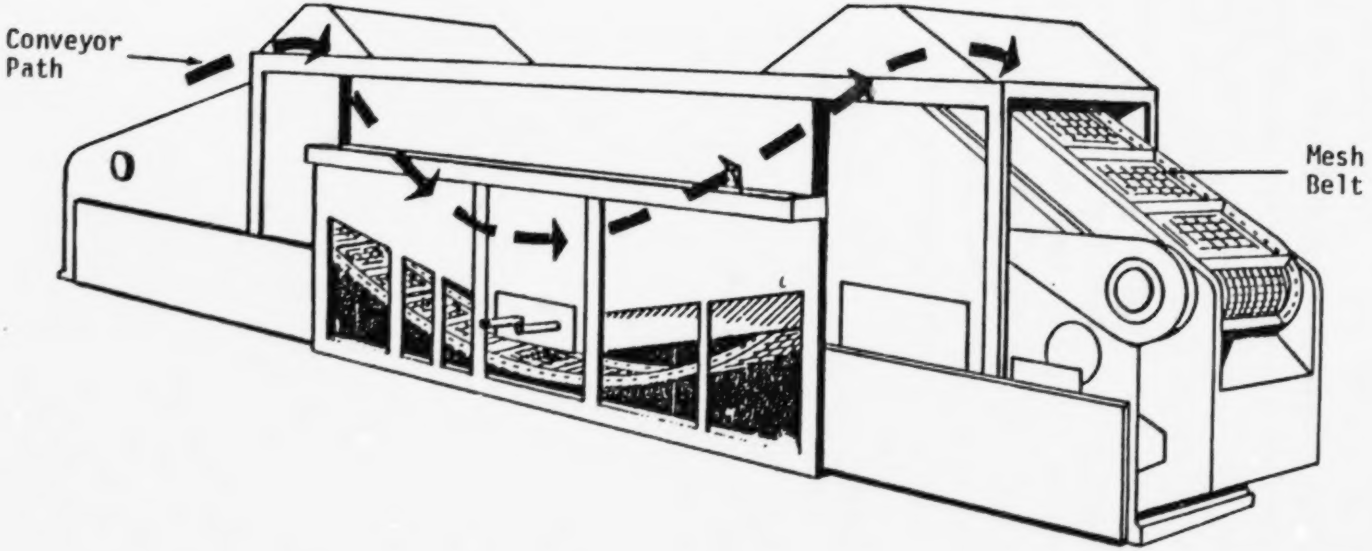


Figure 12. Mesh belt conveyorized degreaser.[41]

not recycled to the process, must be subtracted from the quantity of makeup solvent. One source estimates the average emission rate for a cold cleaner unit is 289 kg per year assuming 2250 hours per year.[43] Emission control technologies and practices employed by organic solvent degreasing and their removal efficiencies are listed in Table 13.

Although chlorobenzenes are expected to contribute to degreaser emissions, it should be noted that significant use of chlorobenzenes as primary degreasing solvents has not been documented. Chlorobenzenes, by themselves, are not used as solvents, but rather, probably only occur in solvent mixtures. Moreover, the quantities of chlorobenzenes used in solvent mixtures are not likely to be very large.[45] The reader is encouraged to contact local plant personnel for information on specific processes, solvent formulations emissions and control technologies.

Source Locations

Organic solvent cleaners which use halogenated solvents are utilized in the production and maintenance of nearly all metal-based commodities. The five principal industries which employ the use of each organic solvent cleaner type are listed in Table 14.

TABLE 13. ORGANIC SOLVENT DEGREASER CONTROL EQUIPMENT[a],[44]

	VOC Emissions During Operation		Control Equipment	
	Source	Percent of Total VOC Emissions	Device	Demonstrated Efficiency (%)
Cold Cleaner	Bath evaporation	20	Cover	92[b]
	Solvent carry-out	25	Drain racks	50
			Ventilation exhaust system to carbon adsorber	60-90
	Waste solvent disposal	55	Holding tank Still Suitable disposal	-- >85% by volume --
Cold Conveyorized Degreaser				
	Bath evaporation Solvent carry-out	85	Entrance & exit area covers Water separator	-- --
			Drying racks Drying tunnel	-- --
			Ventilation exhaust system (including above devices) to carbon adsorber	60
	Waste solvent disposal	15	Still (built-in or external)	--

---

[a] Chlorobenzenes, by themselves, are not used as solvents, but rather, probably only occur in solvent mixtures. Moreover, the quantities of chlorobenzenes used in solvent mixtures are not likely to be very large.[45] Thus, the percent of VOC emissions represented by chlorobenzenes will not be very large.

[b] With cover in place all but 2 hours per day for 5 days per week.

TABLE 14. PRINCIPAL INDUSTRIAL USERS OF ORGANIC SOLVENT CLEANERS - 1980[a],[40]

Standard industrial classification[b]		Estimated no. of cleaners (1980)	Percentage of overall total
I. Cold Cleaners[c]			
753	Auto repair	557,300	51.7
359	Misc. machinery, except electrical	92,200	8.5
354	Metalworking machinery	45,500	4.2
458	Air transport - maintenance	45,500	4.2
356	General industrial machinery	35,900	3.3
	Subtotal	776,400	72.1
	Overall total	1,077,400	100.0
II. Conveyorized Degreasers[c]			
356	General industrial machinery	470	9.4
372	Aircraft and parts	430	8.6
366	Communication equipment	370	7.4
364	Electric lighting and wiring	330	6.6
339	Misc. primary metal products	290	5.8
	Subtotal	1,890	37.9
	Overall total	4,990	100.0

[a] Chlorobenzenes, by themselves, are not used as solvents, but rather, probably only occur in solvent mixtures. Moreover, the quantities of chlorobenzenes used in solvent mixtures are not likely to be very large.[45]

[b] Each industry group is preceded by a 3 digit SIC code which represents that group.

[c] Includes cold cleaners using both halogenated and non-halogenated solvents.

USE OF MONOCHLOROBENZENE AND O-DICHLOROBENZENE AS DYE CARRIERS IN TEXTILE DYEING

Monochlorobenzene (MCB) and o-dichlorobenzene (o-DCB) are effective dye carriers in the coloring of textile products.[11,46] Dye carriers, or dyeing accelerants, are used to promote dye migration and transfer to produce even and satisfactory dyeings. They may be used on cellulose triacetate fibers but are typically used on polyester. The choice of a particular dye carrier often may be based on availability, cost, toxicity, ease of handling, and so on.

Carrier selection is governed primarily by the carrier's boiling point. It must be high enough so that evaporation or steam distillation of the carrier does not occur at the dyeing temperatures, and low enough so that it may be removed from the fabric under plant drying conditions. Since dye carriers have little or no solubility in water, emulsifiers are needed to disperse the carrier in the dye bath. Many carriers are available in the pre-emulsified form. As a general rule, stronger carriers, including phenolic and chlorinated aromatic compounds, are used in open equipment, at a boil, while weaker carriers are used in high temperature dyeing.

Process Description

Dyeing procedures vary with the textile fiber content and the equipment used.[46] Two carrier dyeing procedures for 100 percent polyester fabrics are described below.

Procedure 1 -- The dyebath is prepared by adding water conditioning chemicals for proper water hardness. Dyes are combined with cold water to form a paste which is diluted with warm water (70°C), and then added to the bath containing the fabric. Mixing is initiated for 10 minutes and 5 to 10 grams per liter of carrier are added according to manufacturers instructions. The pH is adjusted to 5 with acetic acid. The bath is brought to a boil over 30 to 45 minutes, boiled for 1 hour, and then cooled slowly. After cooling, the materials are rinsed completely and further processed to remove residual carrier and unfixed dye.

Procedure 2 -- The dye bath is prepared in a similar manner to that presented in procedure 1. After adjusting the pH, both dye dispersant and 1 to 3 grams of carrier per liter of dye bath are added. The temperature is then raised from 50 to 88°C at the rate of 2°C per minute. The equipment is then pressure sealed, and the temperature is raised at the rate of 1°C per minute until it reaches 130°C. This temperature is maintained for 1/2 to 1 hour, depending on the desired shade, and then cooled to 82°C at 1 to 2°C per minute. After depressurization the material is processed as in procedure 1.

Emissions

Possible sources of pollution and control methods for dye carriers are shown in Figure 13. No quantitative emissions data for the textile dyeing industry are available. The reader is encouraged to contact plant personnel to confirm the existence of emissions and control technology to estimate emissions for a specific source.

Source Locations

A listing of the plants involved in the dyeing of cellulose triacetate fibers and polyesters was not available. The Standard Industrial Classification (SIC) codes for establishments engaged in the dyeing of man-made fibers are listed below:

- Broad woven fabrics of man-made fiber - 2262
- Raw stock and narrow fabrics of man-made fiber - 2269.

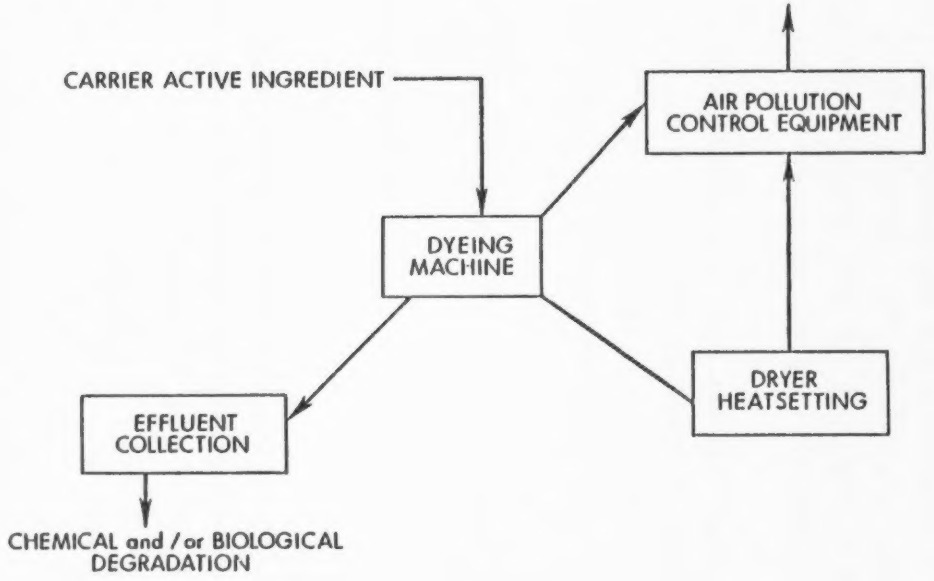

CARRIER ACTIVE INGREDIENT
DYEING MACHINE
AIR POLLUTION CONTROL EQUIPMENT
DRYER HEATSETTING
EFFLUENT COLLECTION
CHEMICAL and / or BIOLOGICAL DEGRADATION

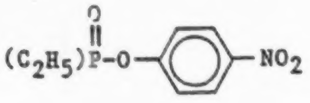
Figure 13. Pollution control equipment - dye carriers.[46]

MANUFACTURE OF CHLORONITROBENZENES FROM MONOCHLOROBENZENE

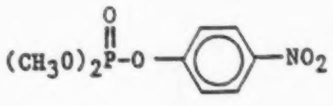
The largest consumption of MCB in the U.S. is in the production of chloronitrobenzenes. Major uses of chloronitrobenzenes are as intermediates in the manufacture of dyes, pigments, and pesticides.

Small amounts of chloronitrobenzenes are used directly as starting materials in dye and pigment production. More often, chloronitrobenzenes are used to produce further dye intermediates, including nitroaniline and phenylenediamine. The o-chloronitrobenzene-derived intermediates shown in Figure 14 are used in the manufacture of specific nitro and thioindigo dyes and pigments and others which could not be identified.

Chloronitrobenzenes also are used in pesticide manufacture to produce other intermediate forms including p-nitroaniline and p-nitrophenol. p-Nitrophenol is necessary in the manufacture of organophosphate pesticides, parathion, and methylparathion.[1]



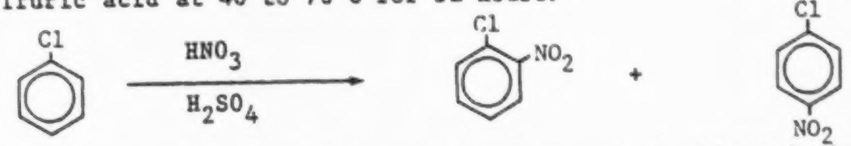
Parathion



Methylparathion

Process Description

Chloronitrobenzenes are manufactured by the nitration of monochlorobenzene using a mixed acid solution of nitric acid and sulfuric acid at 40 to 70°C for 12 hours.[47]



monochlorobenzene 1-chloro-2-nitrobenzene 1-chloro-4-nitrobenzene

Input materials to produce 1 metric ton of combined chloronitrobenzenes include 4536 kg of MCB and 9570 kg of combined 30 to 35 percent nitric acid and 52 to 55 percent sulfuric acid. The product mixture at the end of 12 hours is comprised of (34%) ortho- and (65%) para-chloronitrobenzenes.

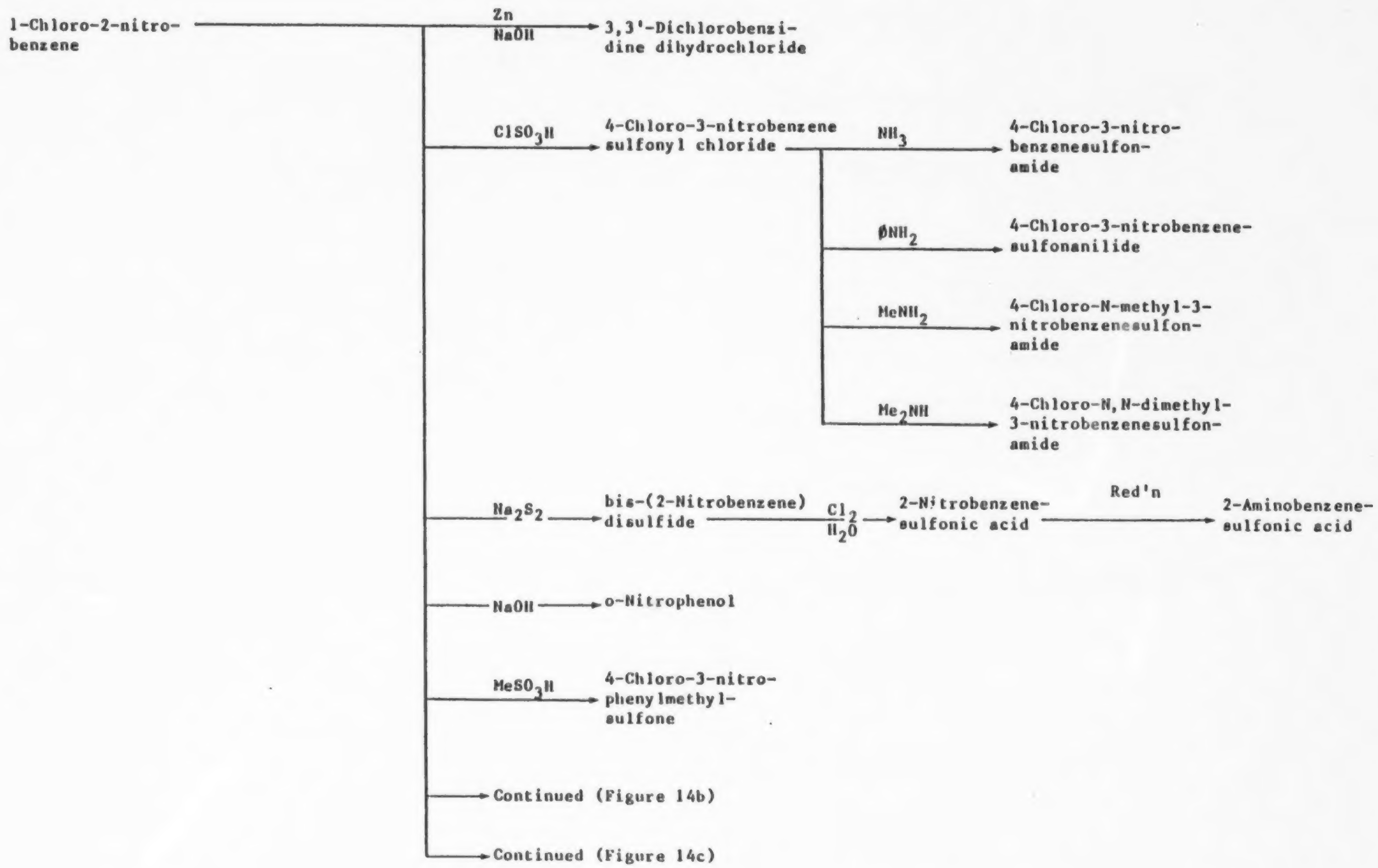

1-Chloro-2-nitrobenzene
Zn
NaOH
3,3'-Dichlorobenzidine dihydrochloride
ClSO$_3$H
4-Chloro-3-nitrobenzene sulfonyl chloride
NH$_3$
4-Chloro-3-nitrobenzenesulfonamide
ØNH$_2$
4-Chloro-3-nitrobenzenesulfonanilide
MeNH$_2$
4-Chloro-N-methyl-3-nitrobenzenesulfonamide
Me$_2$NH
4-Chloro-N,N-dimethyl-3-nitrobenzenesulfonamide
Na$_2$S$_2$
bis-(2-Nitrobenzene) disulfide
Cl$_2$
H$_2$O
2-Nitrobenzenesulfonic acid
Red'n
2-Aminobenzenesulfonic acid
NaOH
o-Nitrophenol
MeSO$_3$H
4-Chloro-3-nitrophenylmethylsulfone
Continued (Figure 14b)
Continued (Figure 14c)

Figure 14a. Synthesis of various intermediates for dye and pigment production from o-chloronitrobenzene.[26]

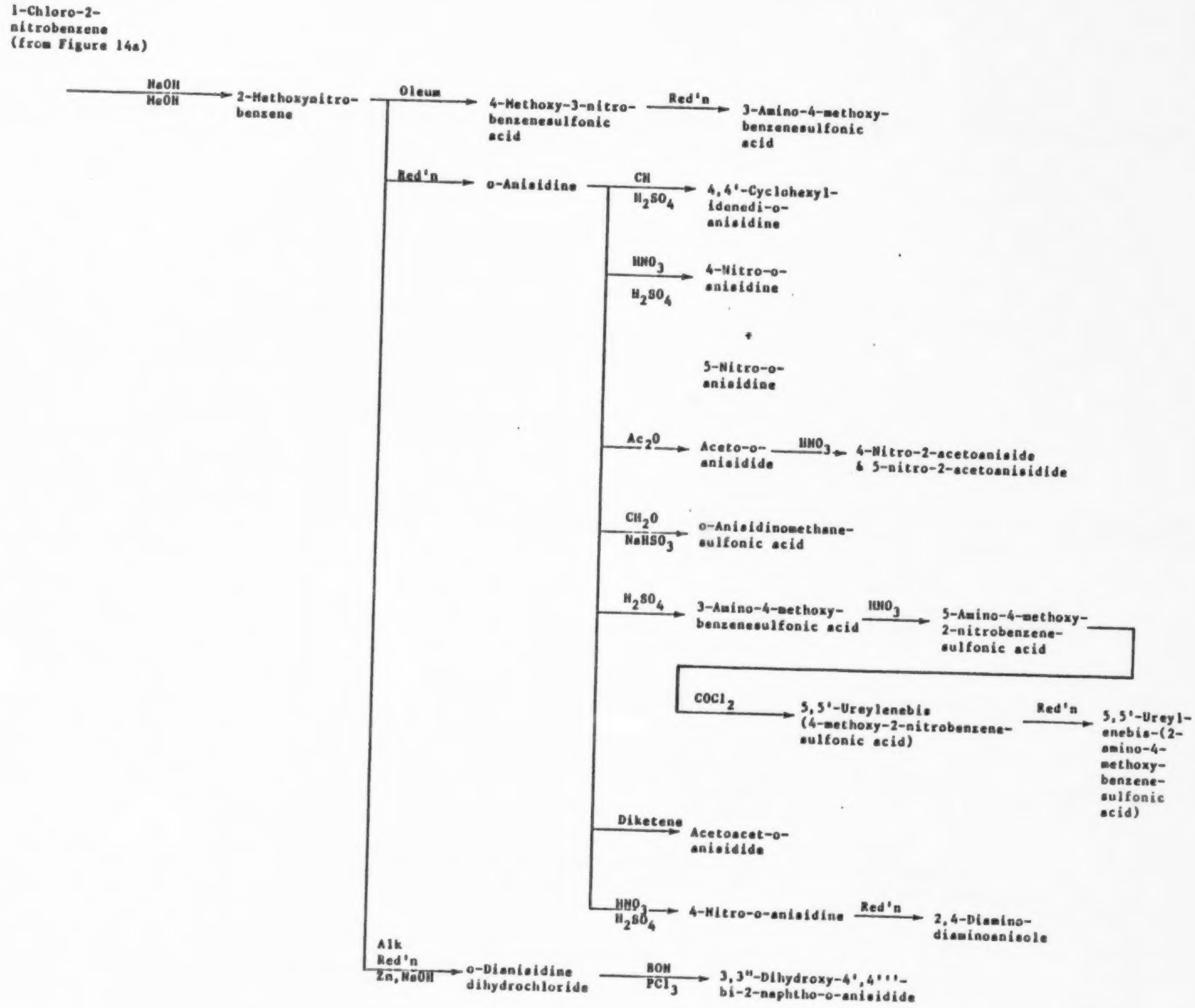

1-Chloro-2-nitrobenzene (from Figure 14a)
NaOH
MeOH
2-Methoxynitrobenzene
Oleum
4-Methoxy-3-nitrobenzenesulfonic acid
Red'n
3-Amino-4-methoxybenzenesulfonic acid
Red'n
o-Anisidine
CH
H2SO4
4,4'-Cyclohexylidenedi-o-anisidine
HNO3
H2SO4
4-Nitro-o-anisidine
+
5-Nitro-o-anisidine
Ac2O
Aceto-o-anisidide
HNO3
4-Nitro-2-acetoaniside & 5-nitro-2-acetoanisidide
CH2O
NaHSO3
o-Anisidinomethanesulfonic acid
H2SO4
3-Amino-4-methoxybenzenesulfonic acid
HNO3
5-Amino-4-methoxy-2-nitrobenzenesulfonic acid
COCl2
5,5'-Ureylenebis (4-methoxy-2-nitrobenzenesulfonic acid)
Red'n
5,5'-Ureylenebis-(2-amino-4-methoxybenzenesulfonic acid)
Diketene
Acetoacet-o-anisidide
HNO3
H2SO4
4-Nitro-o-anisidine
Red'n
2,4-Diamino-diaminoanisole
Alk
Red'n
Zn, NaOH
o-Dianisidine dihydrochloride
BON
PCl3
3,3"-Dihydroxy-4',4'''-bi-2-naphtho-o-anisidide

Figure 14b. Synthesis of various intermediates for dye and pigment production from o-chloronitrobenzene.[26]

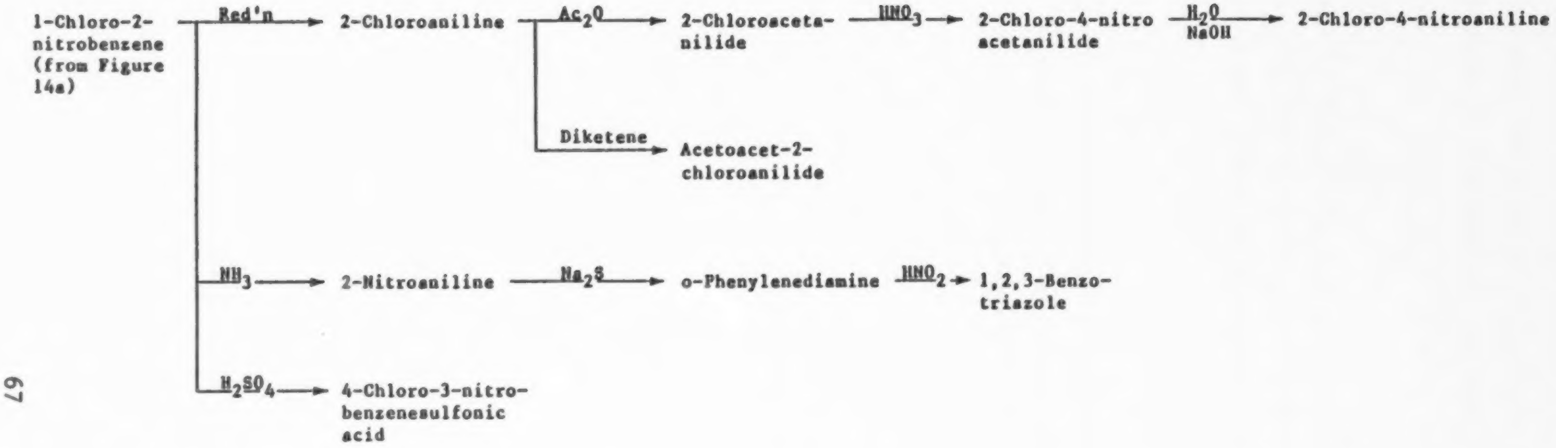


Figure 14c. Synthesis of various intermediates for dye and pigment production from o-chloronitrobenzene.[26]

In the separation process the para- isomer is isolated from the isomer mixture by recrystallization, while the o-chloronitrobenzene is purified by rectification. No further information is available on the manufacturing process.

Emissions

No emissions data are available on the use of MCB in the production of chloronitrobenzenes. The reader is advised to contact plant personnel to identify control technology and emissions for a specific plant process.

Source Locations

p-Chloronitrobenzenes are primarily manufactured by pesticide companies for use as intermediates in their own processes. Table 15 lists producers of o- and p-chloronitrobenzene in the U.S.

TABLE 15. CHEMICAL PRODUCERS OF O- AND P-CHLORONITROBENZENES - 1984[48]

E.I. duPont de Nemours & Company, Inc.
    Chemicals and Pigments Department
    Deepwater, New Jersey

Monsanto Company
    Monsanto Industrial Chemicals Company
    Sauget, Illinois

Note: This listing is subject to change as market conditions change, facility ownership changes, plants are closed, etc. The reader should verify the existence of particular facilities by consulting current listings and/or the plants themselves. The level of chlorobenzene emissions from any given facility is a function of variables such as capacity, throughput and control measures, and should be determined through direct contacts with plant personnel.

MANUFACTURE OF DIPHENYL OXIDE FROM MONOCHLOROBENZENE

Due to its geranium-like odor, diphenyl oxide (also known as phenyl ether) finds its major use in the manufacture of perfumed products, particularly soaps. Other uses are as heat transfer fluids; medicines; resins for laminated electrical insulation; chemical intermediates for such reactions as halogenation, acylation, and alkylation; and dye carriers.

Process Description

Diphenyl oxide is typically produced in a continuous flow tubular reaction system.[49] Chlorobenzene is reacted with aqueous sodium hydroxide (NaOH), and recycled products (containing phenol and sodium phenoxide). These reactants are heated to between 275 and 300°C by passing through a nickel-lined heat exchanger. The reaction temperature of 400°C is achieved electrically and the reactants are allowed to flow through the system for 10 to 30 minutes. The reaction must be maintained at sufficient pressure ($\geq$ 26.2 MPa (258.6 atm)) to prevent vaporization which would allow NaCl, NaOH, or phenoxide to be deposited on the tube walls causing hot spots and excessive corrosion. The resulting two layers from the reaction are: (1) aqueous phenoxide, and (2) an oily layer consisting mainly of diphenyl oxide and unreacted chlorobenzene. Diphenyl oxide is recovered by distillation of this oily layer.

Emissions

Although quantitative estimates are unavailable, only small quantities of MCB are believed to be emitted during the diphenyl oxide manufacturing process. The reader is advised to contact plant personnel for information concerning emissions and control technology employed for specific processes.

Source Locations

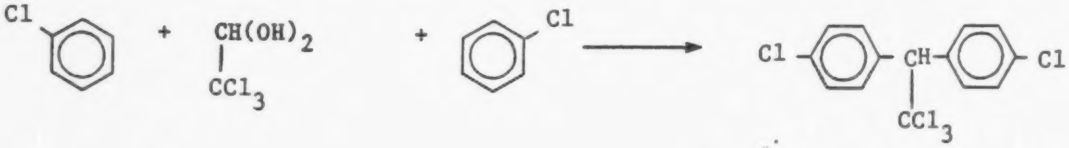
Facilities which are reported in the SRI Directory of Chemical Producers for 1984 as producers of diphenyl oxide are Dow Chemical, U.S.A. of Midland, Michigan and Monsanto Industrial Chemicals Company of Chocolate Bayou, Texas.[50] Monsanto reports that their diphenyl oxide process does not utilize monochlorobenzene.[51] This listing is subject to change as market conditions change, facility ownership changes, plants are closed, etc. The reader should verify the existence of particular facilities by consulting current listings and/or the plants themselves. The level of chlorobenzene emissions from any given facility is a function of variables such as capacity, throughput and control measures, and should be determined through direct contacts with plant personnel.

USE OF MONOCHLOROBENZENE IN THE MANUFACTURE OF DDT

MCB is used in the production of the insecticide dichlorodiphenyltrichloroethane (DDT).

Process Description

DDT is produced by the reaction of chloral (or chloral hydrate) and MCB in the presence of H_2SO_4.[52]



MCB   chloral hydrate   MCB   DDT

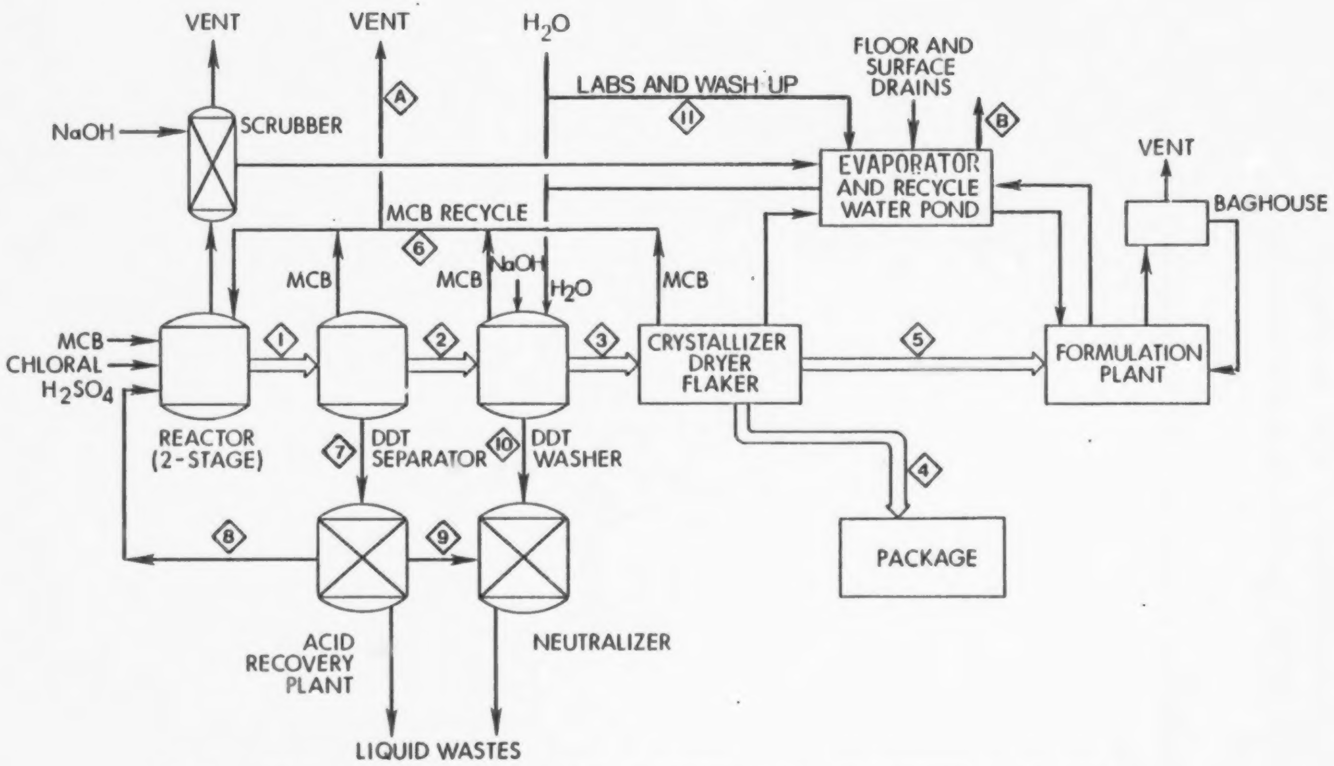
The process illustrated in Figure 15 consists of four basic stages: reaction, separation, processing, and waste control and recovery.

In the "two-stage" reactor, two moles of MCB are reacted with one mole of chloral (with H_2SO_4 as a catalyst) to form DDT. Unprocessed DDT, excess MCB and spent H_2SO_4 (Stream 1) are extracted from the reactor and sent to the DDT separator. DDT (Stream 2) is then washed with sodium hydroxide and water. Final processing of the washed DDT (Stream 3) includes crystallization, drying, or flaking. It is then either packaged (Stream 4) or enters a formulation process (Stream 5).

The DDT process contains three waste recovery steps. One step removes the MCB from the separating and processing streams and recycles it (Stream 6) to the reaction step. The second step removes acid from the separator stream, recycles it (Stream 7) to an acid recovery plant and returns the recovered acid (Stream 8) to the initial reaction step. Waste acid (Stream 9) is combined with dilute caustic from the DDT washer (Stream 10) in a neutralized stage. The final step is recovery of waste from the clean-up operations (Stream 11).[52]

Emissions

Greatest emissions of MCB during DDT production are from the recycling vent (A).[11] Due to the insolubility of MCB in water, emissions are also possible from the evaporator and recycling pond (B).



NOTE: The numbers in this figure refer to process streams, as discussed in the text, and the letters designate process vents. The heavy lines represent final product streams through the process.

Figure 15. Basic operations that may be used in DDT production.[11]

DDT is known to contain monochlorobenzene as an impurity which will be emitted during shipping, handling, and use. Since all DDT produced in the U.S. is exported, DDT-related MCB emissions would only be expected from shipping and handling of DDT. No information was available concerning actual emission rates from these sources.

Source Locations

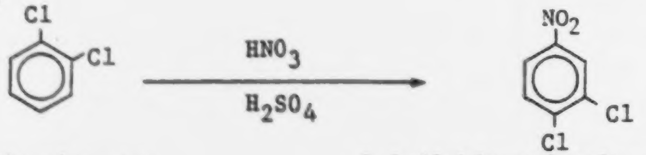
No current information is available on the production sites of DDT in the United States.

MANUFACTURE OF 3,4-DICHLOROANILINE FROM O-DICHLOROBENZENE

An important compound derived from o-DCB is 3,4-dichloroaniline which is used as an intermediate in the production of an anilide pesticide and two substituted urea pesticides. Common names for these pesticides are propanil, diuron, and linuron, respectively. Dow Chemical also cited usage of 3,4-dichloroaniline as an intermediate for polyethers and as a cross-linkage agent in epoxy tar products.[1] Pesticides and production locations are listed in Table 16.

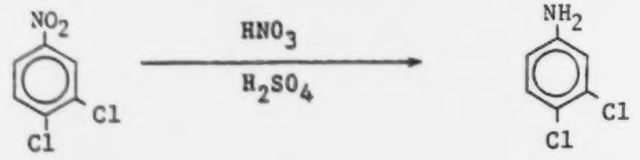
Process Description

Commercially, 3,4-dichloroaniline is prepared by the nitration of o-DCB followed by reduction of the resulting 3,4-dichloronitrobenzene.[56] In many cases, the nitration operation produces two immiscible layers. For safety reasons and ease of operation, atmospheric pressures and temperatures from 0 to 120°C are used. At higher temperatures, competing oxidation reactions become important. Reaction residence times for nitration range from 1 to 60 minutes. The nitration reaction may be written as:



o-dichlorobenzene 3,4-dichloronitrobenzene

The reduction of 3,4-dichloronitrobenzene may be achieved in two ways: (1) by employing iron and HCl; and (2) by using hydrogen and a catalyst with some heating. Other operating parameters are not known. The reduction reaction may be written as:



3,4-dichloronitrobenzene 3,4-dichloroaniline

Emissions

Process, storage, and fugitive emission factors for the production of 3,4-dichloroaniline are given in Table 17. The reader is encouraged

TABLE 16. PESTICIDES USING 3,4-DICHLOROANILINE AS AN INTERMEDIATE - 1984[53,54,55]

	Scientific Name	Common/Registered Brand Names	Producers	Location
Anilide Pesticide	3,4-Dichloropropionanilide	Propanil Rohm and Haas Stam®	Blue Spruce Company Rohm and Haas Company Rohm and Haas Tennessee, Inc. Vertac Chemical	Bound Brook, NJ Knoxville, TN West Helena, AR
Substituted Urea Pesticide	3-[3,4-Dichlorophenyl]-1, 1-dimethylurea	Diuron DCMU DMC DuPont Karmex®	E.I. DuPont de Nemours & Co., Inc. Biochemicals Department	LaPorte, Tx
	3-[3,4-Dichlorophenyl]-1 methoxy-1-methylurea	Linuron Afalon DuPont Lorox®	E.I. DuPont de Nemours & Co., Inc. Biochemicals Department	LaPorte, TX East Chicago, IN

Note: This listing is subject to change as market conditions change, facility ownership changes, plants are closed, etc. The reader should verify the existence of particular facilities by consulting current listings and/or the plants themselves. The level of chlorobenzene emissions from any given facility is a function of variables such as capacity, throughput and control measures, and should be determined through direct contacts with plant personnel.

TABLE 17. EMISSION FACTORS FOR THE PRODUCTION OF 3,4-DICHLOROANILINE[22]

Emission category	kg o-DCB emitted per Mg 3,4-Dichloroaniline produced
Process	1.05
Storage	0.15
Fugitive	0.30
TOTAL	1.50

Note: These emission factors are only general estimates. No information is available on specific emission points included in each emission category, the type of production processes used, or specific control technologies employed, if any. Any given dichloroaniline production plant may vary in configuration and level of control from this hypothetical facility. The reader is encouraged to contact plant personnel to confirm the existence of emitting operations and control technology at a particular facility prior to estimating emissions therefrom.

to contact plant personnel for information regarding actual emissions and control technologies employed at specific locations.

Source Locations

Producers of 3,4-dichloroaniline and their locations are given in Table 18.

TABLE 18. CHEMICAL PRODUCERS OF 3,4-DICHLOROANILINE - 1984[8]

Blue Spruce Company
    Bound Brook, New Jersey

E.I. duPont de Nemours & Company, Inc.
    Chemicals and Pigments Department
        Deep Water, New Jersey

Monsanto Company
    Monsanto Industrial Chemicals Company
        Luling, Louisiana

Note: This listing is subject to change as market conditions change, facility ownership changes, plants are closed, etc. The reader should verify the existence of particular facilities by consulting current listings and/or the plants themselves. The level of chlorobenzene emissions from any given facility is a function of variables such as capacity, throughput and control measures, and should be determined through direct contacts with plant personnel.

USE OF CHLOROBENZENES IN THE MANUFACTURE OF TOLUENE DIISOCYANATE

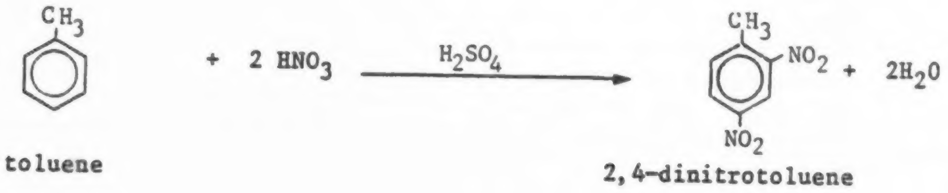
o-DCB and MCB are used in the manufacture of 2,4-toluene diisocyanate (TDI) which is primarily used in the production of urethane.[57] Urethane components derived from TDI are used to manufacture flexible or semi-flexible foams in furniture, bedding, and automotive products and rigid polyurethane foams for use as insulation materials in refrigerators, freezers, and water heaters.[58]

In the TDI manufacturing process described below, o-DCB is used as an inert process solvent. Alternatively, TDI may be produced by a process which utilizes monochlorobenzene; however, no details are available concerning this method.

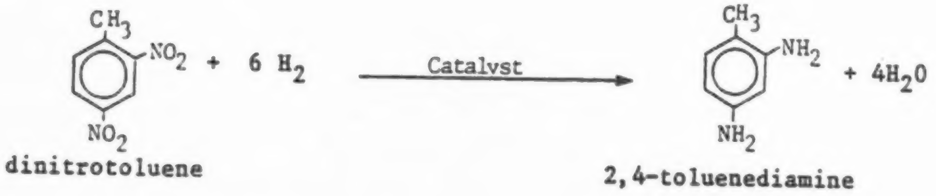
Process Description

TDI is produced by the nitration of toluene followed by the reduction of dinitrotoluene to form 2,4-toluenediamine which is then phosgenated to form TDI.[59] The reaction steps are illustrated below:

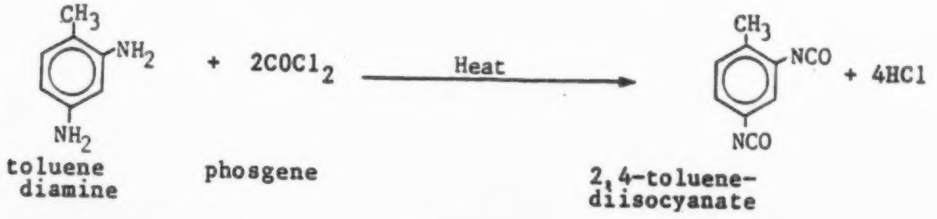
Reaction 1:



Reaction 2:



Reaction 3:



A typical TDI plant operates continuously and is integrated with the production of dinitrotoluene and toluenediamine. The process flow diagram shown in Figure 16 represents a continuous process using toluene, nitric acid, hydrogen, and phosgene as input materials. Only the phosgenation reaction (reaction 3) will be discussed here since it is the only reaction in the TDI process which involves o-DCB.

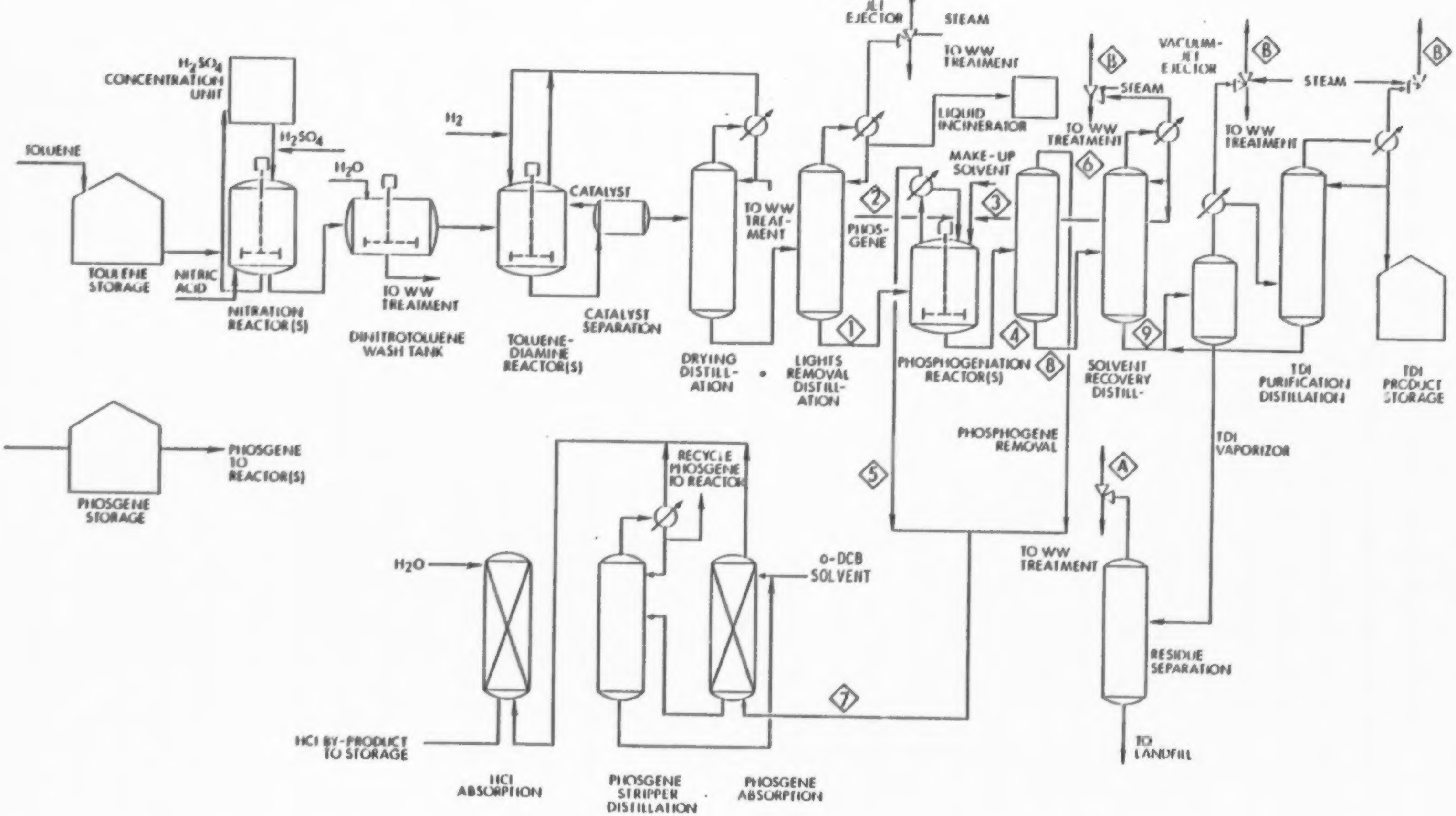
Purified toluene diamine (TDA) (Stream 1) is reacted with phosgene (Stream 2) in the presence of o-DCB solvent (Stream 3) to form crude TDI (Stream 4). Phosgene is condensed out of the by-product HCl and subsequently recycled to the reactor. The HCl that goes overhead from the condenser (Stream 5) may contain trace amounts of phosgene and is therefore sent to the phosgene absorber. The crude TDI mixture from the phosgenation reactor is sent to a distillation column for removal of phosgene. The phosgene overhead (Stream 6) from this distillation and the HCl and trace-phosgene stream (Stream 5) from the reactor condenser are combined (Stream 7) and sent to a column that absorbs phosgene with the o-DCB solvent. The solvent is then stripped of phosgene in a distillation column and recycled to the absorber.[59]

The TDI-DCB solvent mixture (Stream 8) from the phosgene removal distillation column is sent to a vacuum distillation column to recover the DCB solvent overhead, which is then recycled to the phosgenation reactor. The crude TDI (Stream 9) from the bottom of the solvent recovery distillation column is vaporized by flash distillation to separate TDI from any polymeric isocyanates that might have been formed.[59]

The bulk of commercially used TDI is a mixture of 80 percent 2,4-toluene diisocyanate and 20 percent 2,6-toluene diisocyanate. However, a 65:35 mixture and pure 2,4-isomer are also available.

Emissions

Possible o-DCB emissions include the residue separation vacuum jet vent (A) and the vacuum jet vents (B) associated with solvent recovery distillation, TDI flash distillation, and TDI purification distillation.[59] It is estimated that only a small fraction of o-DCB utilized is released into the atmosphere.[45] Allied Chemical reported that in 1978 approximately 1 percent or less of the o-DCB purchased was released.[60]



NOTE: The numbers in this figure refer to process streams, as discussed in the text, and the letters designate process vents.

Figure 16. Basic operations that may be used in toluene diisocyanate production.[59]

Source Locations

Producers of TDI used are listed in Table 19. It is not known whether the producers actually utilize o-DCB or MCB as described above. Olin reports that MCB is used in their TDI production process, a major portion of which is incinerated.[62] BASF reports that "MCB emissions should not be assumed to necessarily result from [its Geismar, LA] TDI operations."[92]

TABLE 19. CHEMICAL PRODUCERS OF TOLUENE DIISOCYANATE - 1984[61]

BASF Wyandotte Corp.
    Polymers Group
        Urethanes Chemicals Business
            Geismar, LA

Dow Chemical U.S.A.
    Freeport, TX

ICI Americas Inc.
    Performance Resin Division
        Rubicon Chemicals, Inc.
            Geismar, LA

Mobay Chemical Corporation
    Polyurethane Division
        Cedar Bayou, TX
        New Martinsville, WV

Olin Corporation
    Olin Chemicals Group
        Lake Charles, LA
        Moundsville, WV

This listing is subject to change as market conditions change, facility ownership changes, plants are closed, etc. The reader should verify the existence of particular facilities by consulting current listings and/or the plants themselves. The level of chlorobenzene emissions from any given facility is a function of variables such as capacity, throughput and control measures, and should be determined through direct contacts with plant personnel.

USE OF O-DICHLOROBENZENE AS A SOLVENT IN PHARMACEUTICAL MANUFACTURING

O-DCB is used as a solvent in the manufacturing of pharmaceutical products by chemical synthesis.

Process Description

Synthetic pharmaceuticals are normally manufactured in a series of batch operations, many of which involve the use of solvents.[63] Figure 17 presents basic operations that may be used in a batch synthesis process. To begin a production cycle, the reactor is washed with water and dried with a solvent. Air or nitrogen is usually used to purge the tank after it is cleaned. Solid reactants and solvent are then charged to the reactor. After the reaction is complete, remaining unreacted volatile compounds and solvents may be distilled off, typically using a water cooled condenser. The pharmaceutical product is then transferred to a holding tank. In the holding tank, the product may be washed three to four times with water or solvent to remove any remaining reactants and byproducts. The solvent used in washing generally is distilled from the reaction product. The crude product may then be dissolved in another solvent and transferred to a crystallizer for purification. After crystallization, the solid material is separated from the remaining solvent by centrifuging. While in the centrifuge, the product cake may be washed several times with water or solvent. Tray, rotary, or fluid-bed dryers are employed for final product finishing.[63]

Emissions

Where o-DCB is used as a solvent in the manufacture of a pharmaceutical product, each step of the manufacturing process may be a source of o-DCB emissions. The magnitude of emissions varies widely within and among operations; therefore, it is impossible to cite typical emission rates for various operations. Based on an industry-wide mass balance, 140 grams of o-DCB per megagram used are emitted directly to the air.[64] Also, 8,300 g/Mg used are estimated to be released as sewage. Some of this o-DCB will volatilize subsequent to discharge creating a secondary source of emissions.

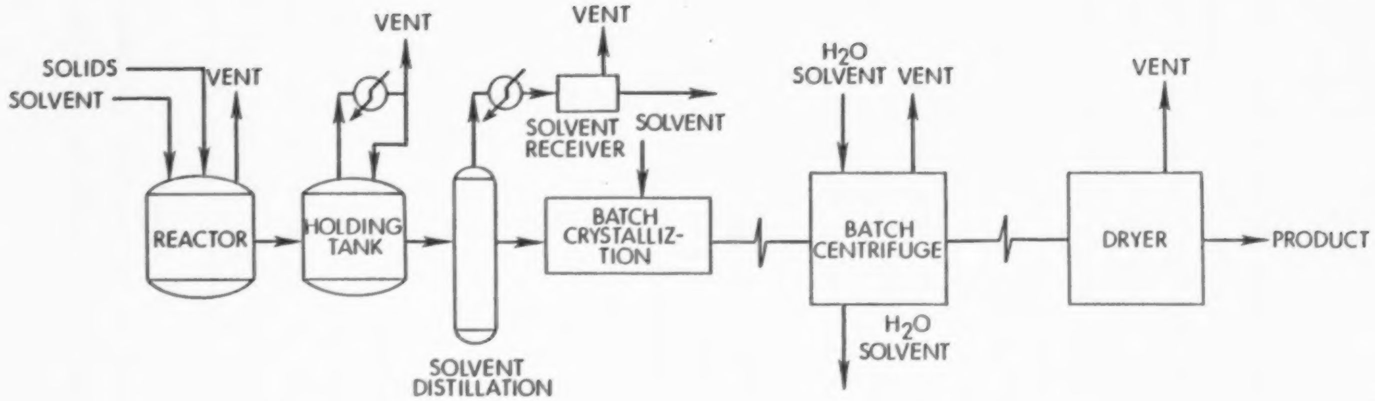


Figure 17. Basic operations that may be used in pharmaceutical manufacturing.[63]

An approximate ranking of emission sources has been established and is presented below in order of decreasing emission significance. The first four sources typically account for the majority of emissions from a plant.[63]

- Dryers
- Reactors
- Distillation units
- Storage and transfer
- Filters
- Extractors
- Centrifuges
- Crystallizers

Condensers, scrubbers, and carbon adsorbers can be used to control emissions from all of the above emission sources. Storage and transfer emissions can also be controlled by the use of vapor return lines, conservation vents, vent scrubbers, pressurized storage tanks, and floating roof storage tanks.

Source Locations

The Standard Industrial Classification (SIC) code for pharmaceutical preparations is 2834. There are approximately 800 pharmaceutical plants producing drugs in the United States and its territories. Most of the plants are small and have less than 25 employees. Nearly 50 percent of the plants are located in 5 states: 12 percent in New York, 12 percent in California, 10 percent in New Jersey, 5 percent in Illinois, and 6 percent in Pennsylvania. These states also contain the largest plants in the industry. Puerto Rico has the greatest growth in the past 15 years, during which 40 plants have located there. Puerto Rico now contains 90 plants or about 7.5 percent of the total.[63]

USE OF P-DICHLOROBENZENE AS A SPACE DEODORANT

The majority of p-DCB produced in the United States has a non-intermediate dispersive use in space, toilet bowl, and garbage deodorants. Due to its volatility, density, pleasant odor, and solid nature at room temperature, it is used alone or in combination with disinfectant substances to produce deodorants in a variety of continuous evaporation forms, most commonly solid air deodorizers and toilet blocks.

Process Description

p-DCB derived deodorant products contain up to 100 percent p-DCB with the addition of a perfume in some cases. Limited information was available detailing the processes by which the deodorant types are manufactured. However, most solid block deodorants are formed by combining the active ingredients such as p-DCB with a carrier substance.[65] The most common carrier for all types of deodorants is water; however, other carriers such as process oils, solvents, and various petroleum products are also employed depending on the form of the deodorant. In solid and semisolid products, active ingredients are incorporated into sublimable water based gels, waxy solids, or powder form. The process by which active substances are incorporated into toilet blocks is assumed to be similar in nature.

Emissions

It is estimated that all p-DCB incorporated into solid space and garbage deodorants will enter the atmosphere by sublimation during production or use. Use of toilet bowl deodorizers is expected to contribute only minor amounts of p-DCB, the balance entering the sewerage.[38]

Source Locations

For 1984, 33 percent of U. S. p-DCB production is expected to be used in the manufacture of space deodorants.[11] Information concerning specific manufacturers was not available. Users of p-DCB-based deodorant products include the industrial, commercial, and consumer sectors.

USE OF P-DICHLOROBENZENE IN MOTH CONTROL

p-DCB is used in consumer, commercial, and industrial sectors in different applications for moth control. p-DCB formulated into cakes, blocks and balls contain greater than 99 percent p-DCB.[38] Information on manufacture of these products is not available.

Commercial applications of moth control products include preservation of glycerin treated dried flowers during storage and handling and moth proofing of textiles during production.[38] p-DCB is applied to the textiles during the dyeing operation and then may be fixed in the fibers by chemical reactions with a protein.[66] It may also be sprayed onto fabric combined with a volatile solvent.

Emissions

All p-DCB used in moth control products and applications is expected to be emitted to the atmosphere by sublimation during production or use.[38]

Source Location

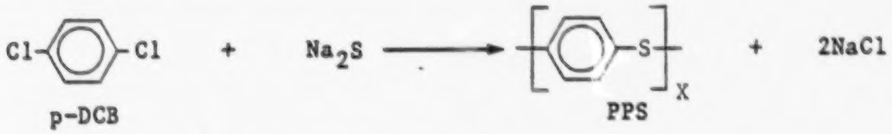
Uses of moth control agents are too widespread to categorize. Manufacturers of moth control agents containing p-DCB were not identifiable due to limited information.

USE OF P-DICHLOROBENZENE IN THE PRODUCTION OF POLYPHENYLENE SULFIDE

p-DCB is used in the production of polyphenylene sulfide, a commercial polymer with many industrial applications. Characteristics of polyphenyl sulfide, also named polythio-1,4-phenylene, or PPS, include: good thermal stability, retention of mechanical properties at elevated temperatures, excellent chemical resistance, and an affinity for a variety of fillers.[67] It is also in a class of polymers with high dielectric strength useful for insulation applications. PPS has a variety of industrial applications for molded parts including nonlubricated bearings, seals, pistons, impellers, pump vanes and electronic components. It can also be applied as a coating to metals and ceramics as a protective and corrosion resistant medium for equipment in the chemical and petroleum industries. When mixed with small amounts of polytetrafluoroethylene, it provides a non-stick surface in cookware and other industrial applications.

Process Description

PPS is formed by the following reaction of p-DCB and sodium sulfide in a polar solvent.



Steps involved in the manufacture of PPS shown in Figure 18 are: (1) preparation of sodium sulfide from aqueous caustic and aqueous sodium hydrosulfide in a polar solvent, (2) dehydration by distillation of the above feedstock, (3) polymer formation from the reaction of the sodium sulfide stream and p-DCB at an elevated temperature in a polar solvent, (4) polymer recovery, (5) removal of by-product sodium chloride by washing, (6) drying and (7) packaging.[68] The product of the above process can be used in coating applications by slurry-coating procedures; however, most often it is used as a feedstock in the production of molding-grade resins.

Molding-grade resins are produced by a curing process in which the virgin polymer is exposed to a small amount of air at a high

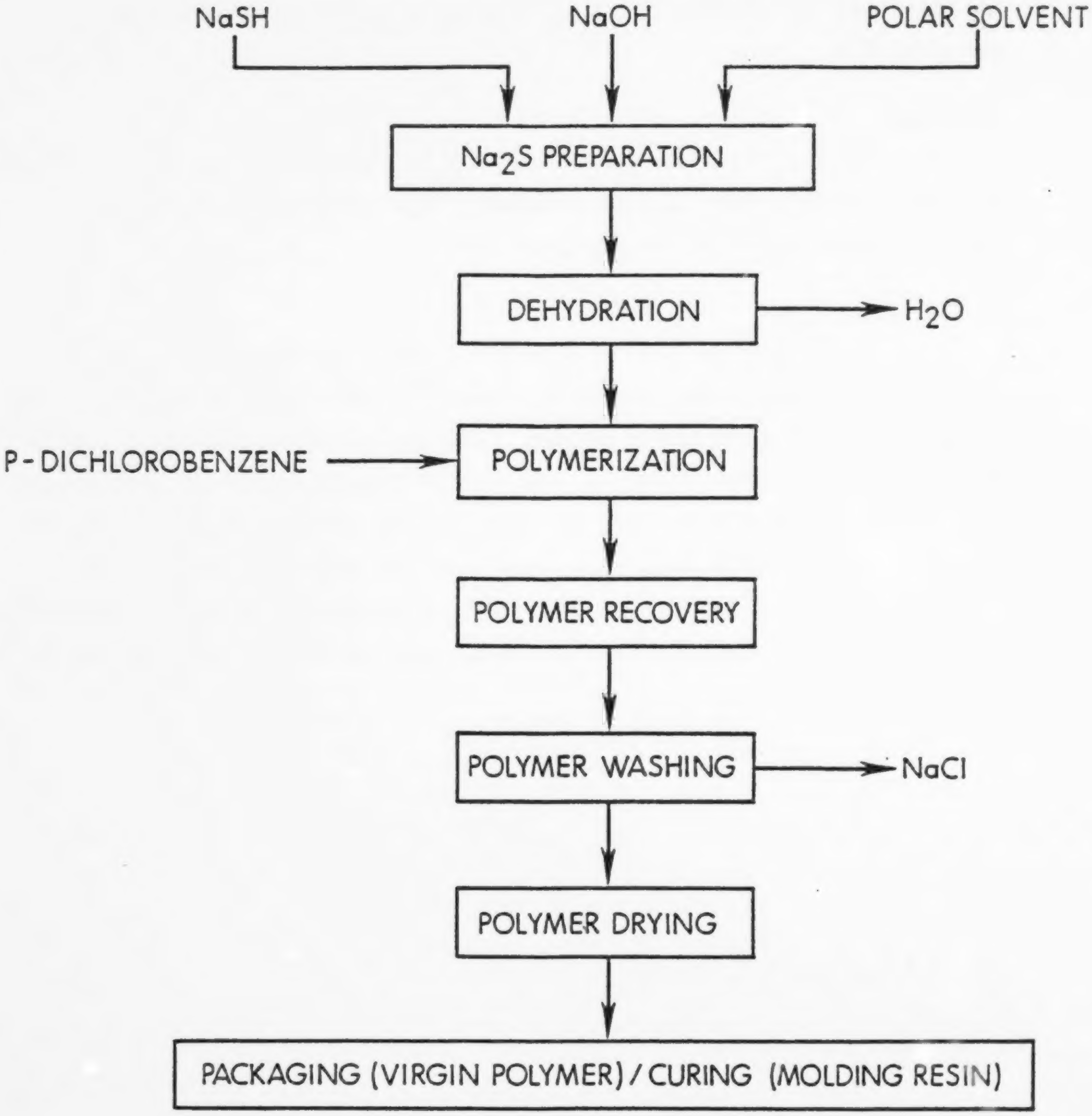


Figure 18. Process flow diagram of PPS manufacture.[68]

temperature. At this point, a higher molecular weight resin is produced while lower molecular weight oligomers are volatilized. Residence time, reaction temperature, and melt viscosity are important in the formation of various grades of PPS. The cured polymer is cooled, combined with fillers (such as glass fibers, if desired), pelletized, and then packaged.[68]

Emissions

No emissions data are available for the production of polyphenylene sulfide. To determine actual emissions from particular processes, specific plants should be contacted.

Source Locations

Polyphenylene sulfide is produced by Phillips Petroleum at facilities in Borger and Pasedena, Texas.[69] This listing is subject to change as market conditions change, facility ownership changes, plants are closed, etc. The reader should verify the existence of particular facilities by consulting current listings and/or the plants themselves. The level of chlorobenzene emissions from any given facility is a function of variables such as capacity, throughput and control measures, and should be determined through direct contacts with plant personnel.

USE OF DICHLOROBENZENES IN PESTICIDES

Both o- and p-DCB are listed in the Farm Chemicals Handbook for agricultural application.[70] In addition to moth control, p-DCB is used in tobacco seed beds for blue mold control, peach tree borer control and to prevent mildew and mold on leather and fabrics. o-DCB has more widespread use as an herbicide, insecticide and soil fumigant effective in control of peach tree borers, bark beetles and grubs, mites, termites and insects in poultry houses and animal sleeping quarters.

Pesticides are most commonly used in the forms of dusts, water dispersion, emulsions, and solutions depending on the type of control required. Active ingredients are combined with accessory agents (such as dust carriers, solvents, emulsifiers, wetting and dispersing agents, deodorants or masking agents) to form dusts, wettable powders, granulars, emulsives, baits and slow release formulations. The above formulations are generally applied by three methods determined by the type of carrier used: (1) spraying (with a water or volatile oil carrier), (2) dusting (with a fine powder carrier), or (3) fumigation (in which the formulation is applied as a gas).[71] Information was not available for specific application procedures or formulation processes of DCBs.

Emissions

No information was available concerning emissions from formulation processes or application of specific pesticide formulations. It is assumed that all DCBs used in pesticide applications are released to the atmosphere at a rate depending on volatility and application form. An estimate of emissions for regional pesticide formulation sites is given in Table 20.

Source Locations

Information on formulators of pesticides containing DCBs was not available. Limited information was available on the current location of DCBs pesticide use.

TABLE 20. 1978 REGIONAL DICHLOROBENZENE EMISSIONS ESTIMATES FROM PESTICIDE FORMULATION (kg/yr)[72]

Region	Sites	1978 Emissions o-DCB (kg/yr)	 p-DCB (kg/yr)
New England	4	20	36
Mid Atlantic	37	181	331
East North Central	19	92	170
West North Central	15	72	134
South Atlantic	17	84	152
East South Atlantic	14	68	125
West South Atlantic	15	73	134
Mountain	5	25	45
Pacific	13	64	116
Total	139	680	635

USE OF CHLOROBENZENES IN BONDED ABRASIVE PRODUCTS MANUFACTURE

The abrasives industry employs small amounts of p-DCB and 1,2,4-TCB in the production of ceramic- and resinoid-bonded products in the shape of wheels, discs, sticks, blocks and segments.

Process Description

The first step in bonded abrasives manufacture is the combining of abrasive grain materials (such as aluminum oxide, silicon carbide, and/or diamond grains), wetting agents (of which some or all consist of 1,2,4-TCB) and bonding materials in large kettle type machines resembling bakery dough mixers.[73] Ceramic bonding materials include feldspar, frit and clays selected for their fusibility. After mixing, measured amounts are poured into slightly oversized molds, compressed in hydraulic presses, and then dried under constant humidity. The forms are then fired in bell, periodic, or continuous kilns for several days at temperatures up to 1260°C.

The same process is used in making resinoid-bonded wheels; however, lower curing temperatures of 150 to 200°C are used. If a more porous structure is desired, p-DCB is added during mixing. p-DCB is used as an additive because as a solid it can be crushed into definable grit size. During the curing process, the p-DCB volatilizes, leaving pores and wide grain spacing.

Emissions

Small amounts of p-DCB and TCB are released in the formulation and mixing of process constituents in abrasives manufacture; however, most of these substances volatilizes during the curing process. As a result, emissions from the use of the finished products are negligible.[39]

Source Locations

No information was available on abrasive or grinding wheel producers which use p-DCB or 1,2,4-TCB in the manufacturing process.

USE OF CHLOROBENZENES IN WOOD PRESERVATIVES

DCB and TCB isomers are used as repellents and wood preservatives against termites, powder-post beetles, and carpenter ants. The chlorobenzene products are applied on surfaces or injected into standing wood buildings.[39] The DCB technical wood preservative product contains a mixture of 75 to 85 percent o-DCB and 15 to 25 percent dissolved p-DCB. The technical product of TCB contains 1,2,4-TCB and a small amount of the 1,2,3-TCB isomer. No information was found on the formulation process or application practices.

Emissions

Approximately 1 percent of 1,2,4-TCB is estimated to be emitted to the atmosphere during application and handling, the balance remaining in the wood.[39] Emissions factors for DCBs and 1,2,3-TCB have not been reported.

Source Locations

The formulations and users of wood preservatives and products containing chlorinated benzenes are not identified in the literature.

USE OF 1,2,4-TRICHLOROBENZENE AS A DYE CARRIER IN THE TEXTILE DYEING INDUSTRY

The most widely known use of 1,2,4-TCB is that of a dye carrier in textile dyeing operations. Textile mill operations which use 1,2,4-TCB include wool scouring, woven fabric finishing (simple and complex processing with desizing), and knit fabric finishing. In most cases 1,2,4-TCB dye carrier is used only when specific (usually darker) hues are required in man-made fibers.

Process Description

When used as a dye carrier, 1,2,4-TCB is combined with a disperse dye and a leveling agent, and then applied to the material at 100°C for several hours.[39] Typically, the amount of TCB contained in the dye carrier formulation ranges from 10 percent to 90 percent of the total formulation or from less than 2 percent to 10 percent by weight, once added to the bath. At this point, excess carrier is removed by either (a) alkaline scour at 70° to 80°C with sulfated fatty alcohol, or (b) rinsing the material followed by heating to 190°C for one minute. General process and equipment for use of dye carriers are described in the section entitled Use of Monochlorobenzene and o-Dichlorobenzene as Dye Carriers in Textile Dyeing.

Emissions

It is estimated that all of the 1,2,4-TCB contained in the dyeing solutions is released to the environment.[39] A small quantity is emitted to the atmosphere during the removal of excess solution from the material by evaporation. The majority of 1,2,4-TCB is discharged to the waste water stream in the release of spent dye solution and alkaline scouring wastes. Due to the volatility of 1,2,4-TCB in water, secondary emissions from the waste water stream are possible.

Wet processing textile mills employ various levels of available control technologies which may remove TCBs from the waste water. In Table 21, levels of control technology are shown with the estimates of quantities of TCB emitted for wool scouring, woven fabric finishing and knit fabric finishing processes. Preliminary waste water treatments include neutralization, screening, equalization, heat exchange,

TABLE 21. 1,2,4-TCB EMISSIONS FROM SPECIFIC WATER TREATMENT PROCESSES IN WET PROCESSING TEXTILE MILLS - 1979 (MEGAGRAMS)[39]

Textile Operation	Wool Scouring						Woven Fabric Finishing						Knit Fabric Finishing					
			Quantity Released (Mg)[a]						Quantity Released (Mg)[a]						Quantity Released (Mg)[a]			
			Water[b]						Water[b]						Water[b]			
Type of Treatment	% of total TCB-containing wastes	TCB-containing wastes (Mg)	Direct	Indirect	Air[c]	Land	% of total TCB-containing wastes	TCB-containing wastes (Mg)	Direct	Indirect	Air[c]	Land	% of total TCB-containing wastes	TCB-containing wastes (Mg)	Direct	Indirect	Air[c]	Land
None	35	37	6	31	--	--	41	615	41	574	--	--	51	961	66	895	--	--
Preliminary	29	30	12	18	--	--	22	330	34	296	--	--	21	396	--	396	--	--
Biological or Equivalent	35	38	3	1	17[d]	17[d]	25	375	28	10	169[d]	169[d]	20	377	21	17	169[d]	169[d]
Advanced	0	0	--	--	--	--	1	15	--	--	--	15	2	38	--	--	--	38
Unknown	0	0	--	--	--	--	11	165	132	33	--	--	6	113	92	21	--	--
TOTAL	99	105	21	50	17	17	100	1501	235	913	169	184	100	1885	283	1225	169	207

[a] Quantities released to each media are added to equal the number in the previous "TCB-containing wastes" columns.

[b] After treatment waste water is discharged directly into surface water or enters a publicly-owned treatment work (indirect).

[c] Does not include emissions due to volatilization from waste water subsequent to discharge.

[d] Assumes that 1,2,4-TCB removed during waste water treatment when sent to land was equally divided between air and land.

disinfection, primary sedimentation, and/or floatation. Further treatment in wet mills may include the use of aerated and unaerated lagoons, biological filtration, activated sludge, and chemical coagulation/flocculation. Advanced treatment refers to the use of activated carbon, chemical coagulation, ozonation, filtration, ion exchange and membrane processes. These waste water treatment processes may result in the release of 1,2,4-TCB into the atmosphere.

In a 1979 EPA survey, it was estimated that 3,490 Mg of 1,2,4-TCB were used by domestic textile mills.[39] Assuming that the survey is representative of the entire textile industry (which is estimated to consist of 2,000 wet processing mills), and that each operation used a proportional quantity, then it is calculated that 3, 43, and 54 percent of the total 3,490 Mg of TCB, or 105, 1501, and 1885 Mg, were used by wool scouring, woven fabric finishing, and knit operations, respectively.

Source Locations

A listing of the plants involved in the dyeing of man-made fibers was not available. The Standard Industrial Classification (SIC) codes for these establishments are listed below:

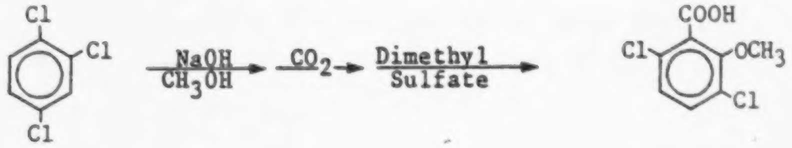
- Broad woven fabrics of man-made fiber - 2262
- Raw stock and narrow fabrics of man-made fiber - 2269.

USE OF 1,2,4-TRICHLOROBENZENE IN THE MANUFACTURE OF PESTICIDE INTERMEDIATES

TCB is used as an intermediate in the production of dicamba (herbicide), stirofos (insecticide), trichloro-nitrobenzene (fungicide), and 2,5-dichlorobenzoic acid (herbicide).[39] It is also possible to produce the herbicide chloramben from 2,5-dichlorobenzoic acid.

Process Descriptions

1,2,4-TCB is used to produce dicamba (3,6-dichlorolo-anisic acid, 3,6-dichloro-2-methoxybenzoic acid) by what is known as the dicamba process.[39]

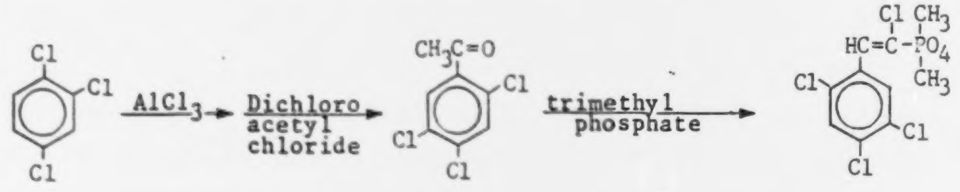


1,2,4-TCB

dicamba

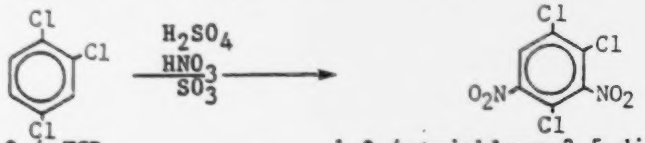
In the process, TCB and sodium hydroxide are dissolved in methanol in the presence of carbon dioxide and dimethyl sulfate and heated to 190°C for 4 hours in a bomb. The resultant mixture is cooled, filtered, dryed, and further processed to make dicamba.

Stirofos, or 2-chloro-1-(2,4,5-trichlorophenyl) ethenyl dimethyl phosphate, is produced by reacting 1,2,4-TCB with aluminum chloride.[39] Dichloroacetyl chloride is stirred into the mixture, heated slowly to 90°C and maintained for 4 hours. The reaction mixture is then poured into an ice and hydrochloric acid solution and extracted with ether. The organic layer is washed successively with diluted hydrochloric acid, water, sodium bicarbonate solution, and saturated sodium chloride solution. Solvent is separated by evaporation and residue is distilled to produce 2,2,2',4',5'-pentachloroacetophenone, which is reacted with trimethyl chloride to yield the herbicide stirofos.



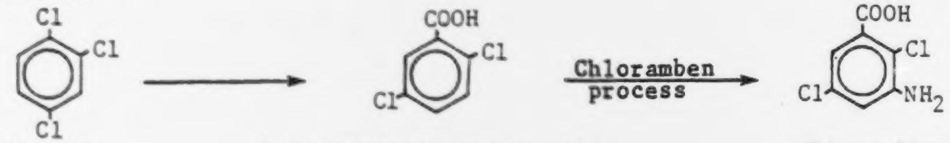
1,2,4-TCB pentachloroacetophenone stirofos

Trichloronitrobenzene is produced by the nitration of TCB with a nitrating solution of 18 percent nitric acid, 73 percent sulfuric acid and 9 percent sulfur trioxide.[39] Initially, the nitrating agent is heated to 35°C and then added to the TCB while stirring. The reaction temperature is held at 110°C for 6.5 hours after which time the reaction mixture is poured into water. Immediate precipitation produces a yield of 90.5 percent of 1,2,4-trichloro-3,5-dinitrobenzene.



1,2,4-TCB 1,2,4-trichloro-3,5-dinitrobenzene

1,2,4-TCB also reacts with cuprous cyanide to form 2,4-dichlorophenyl nitrile which undergoes hydrolysis to produce the herbicide, 2,5-dichlorobenzoic acid.[39] 2,5-Dichlorobenzene may also be used as an intermediate to produce the herbicide, Chloramben, using the Chloramben process.



1,2,4 TCB 2,5-dichlorobenzoic acid Chloramben

No further information is available on the chloramben process.

Emissions

An estimated 33 percent of the total quantity of the TCB used by the pesticide industry was converted or consumed during the manufacturing process. Furthermore, based on process descriptions, approximately 1 percent of the TCB used was released into the environment, of which two-thirds was discharged to air.[39]

In the first step of dicamba manufacture, 90 percent of 1,2,4-TCB is consumed in production of 2,4-dichlorophenyl. The remaining 10 percent is assumed to be released into the environment, most of which is probably converted to other compounds by side reactions. Less than 1 percent used for dicamba production was released to the air in the form of fugitive and handling emissions.[39]

Stirofos production incorporates 77 percent of the TCB into the end product, leaving a possibility of 23 percent being released into the environment. However, much of this 23 percent further undergoes side reactions while some is recycled, resulting in less than 1 percent of TCB being released into the air by fugitive and handling emissions.[39]

In trichloronitrobenzene formulation, 91 percent of TCB is consumed into the end product, and a negligible proportion is discharged to air.[39]

No information was available on emissions from the production of 2,5-dinitrobenzoic acid or chloramben. For actual emissions and control technologies used at a specific plant, contact with appropriate plant personnel is advised.

Source Locations

Producers of TCB-derived pesticides and their locations are shown in Table 22 where information was available. Production information was not obtained for trichloronitrobenzene. The Standard Industrial Classification (SIC) code for pesticide production is 2879.

TABLE 22. CHEMICAL PRODUCERS OF TCB-DERIVED PESTICIDES - 1977[74]

Dicamba	aka 3,6-Dichloro-o-anisic Acid 3,6-Dichloro-2-methoxybenzoic Acid Banvel® D Northwest Industries Inc. Vesicol Chemical Corporation Subsidiary Chattanooga, Tennessee Trimec® PBI-Gordon Corporation Kansas City, Kansas
Stirofos	aka 2-chloro-1-(2,4,5-trichlorophenyl)-vinyl dimethyl sulfate 2-chloro-1-(2,4,5-trichlorophenyl)-ethenyl dimethyl sulfate Gardona® Shell Chemical Company Agricultural Division Mobile, Alabama
Chloromben	aka 3-amino-2,5-dichlorobenzoic acid Verbigen® GAF Corporation Chemical Division Texas City, Texas Amiben® Rorer/Amchem Amchem Products Incorporated Ambler, Pennsylvania Piedmont, California St. Joseph, Missouri Union Carbide Corporation[75] Agricultural Products Group Clinton, Iowa Texas City, Texas Woodbine, New Jersey

Note: This listing is subject to change as market conditions change, facility ownership changes, plants are closed, etc. The reader should verify the existence of particular facilities by consulting current listings and/or the plants themselves. The level of chlorobenzene emissions from any given facility is a function of variables such as capacity, throughput and control measures, and should be determined through direct contacts with plant personnel.

USE OF 1,2,4-TRICHLOROBENZENE IN FUNCTIONAL FLUIDS

Approximately 18 percent of 1,2,4-TCB production is used in formulations of functional fluids such as dielectric liquids and transformer oils. The fluids are standardized mixtures of TCB and polychlorinated biphenyls (PCBs) primarily used in electrical apparatus such as capacitors and transformers. Functional fluids, also called askarels, differ slightly in composition depending on the type of electrical equipment in which they are used.[39] Addition of TCB to PCB lowers the viscosity of the mixture. Askarels are used in electrical equipment because they are non-flammable, chemically stable, have a low vapor pressure and a high dielectric constant. Capacitors use an askarel mixture with a dielectric constant similar to the capacitor paper in order to create a homogeneous electric field. Use of these fluids has been phasing out due to the voluntary halt in production of their PCB constituents in October 1977.

Process Description

During the manufacture of electrical apparatus, liquid dielectric with TCB concentrations ranging from 0.3 to 20 percent by weight is injected through small seal holes in the casings.[39]

Emissions

Very limited amounts of trichlorobenzene are believed to be lost during manufacture of electrical apparatus. One estimate suggests that less than 1 percent of the total 1,2,4-TCB impregnated into the apparatus is introduced to the environment, half of which is emitted into the air as fugitive emissions.[39] Fluids contained within electrical equipment in use are isolated from the environment; however, emissions may occur upon leakage or rupture of the equipment.

Due to the past use of TCBs in transformer fluid mixtures, TCB emissions are possible from the disposal or destruction of PCB-contaminated materials. Contaminated materials include: PCB fluids, PCB articles (items which contain PCBs and whose surface(s) have been in direct contact with PCBs) and PCB containers (barrels, drums, containers, etc., that contain PCBs and whose surfaces have been in direct contact with PCBs).[76] Under current regulations, PCB contaminated equipment and fluids are required to be disposed of by incinerator, high efficiency boiler, chemical waste landfill, or other approved disposal methods. Selection of disposal/destruction method is determined by the concentration of PCBs contained in the materials.

At one electrical wire insulation incinerator, trichlorobenzene and tetrachlorobenzene emissions have been measured to be less than 0.5 mg/hr and 0.3 mg/hr, respectively, during normal operation.[77] The facility utilized waste transformer oil containing less than 50 ppm PCBs as fuel, and burned off the insulation from aluminum and copper windings of non-rebuildable transformers. The incinerator employed both primary and secondary combustion chambers and an afterburner.

No specific information was available detailing emissions from high efficiency boilers, landfills or other disposal technologies. However, negligible amounts of TCB are expected to volatilize over time as a result of landfilling of PCB contaminated apparatus.

For data on specific source emissions and control technologies, contact should be made with personnel at individual plants.

Source Locations

Approximately 18 percent of the total 1,2,4-TCB production is used in synthetic transformer oil and dielectric fluids.[39] No information concerning locations of transformer oil and dielectric fluids producers was available.

As of July 1984, four commercial incinerators, eight industrial incinerators and two mobile incinerators have been approved for the destruction of PCB materials. The commercial units include those operated by Rollins Environmental Services in Deer Park, Texas; Energy Systems Company (ENSCO) in El Dorado, Arkansas; General Electric Company in Pittsfield, Massachusetts; and SCA in Chicago, Illinois. The industrial PCB incinerators are operated by the General Electric Company in Waterford, New York; by Dow Chemical in Freeport, Texas; Oyster Creek, Texas; and Plaquemine, Louisiana; by Vulcan Materials in Geismar, Louisiana; by PPG in Lake Charles, Louisiana; by LaPort Chemical Corporation in Pasadena, Texas; and by Los Alamos Scientific in Los

Alamos, New Mexico. The mobile incineration systems are operated by EPA, Edison, New Jersey; and Pyro-Magnetics, Tullahoma, Tennessee.[78,79]

Specific locations of other incinerators which may be used for destruction of electrical apparatus containing TCB or PCB fluids were not identified in the literature. However, the source classification code (SCC) for incineration of industrial wastes in EPA's National Emissions Data System is 5-03-001-xx.[80] The reader should verify the existence of particular facilities by consulting the plants themselves.

HEXACHLOROBENZENE GENERATION DURING CHLORINATED SOLVENT PRODUCTION

Approximately 60 percent of the total national HCB waste load is attributable to chlorinated solvent production, primarily from the production of carbon tetrachloride, trichloroethylene, and perchloroethylene. Of these, perchloroethylene production is expected to produce the greatest quantity. The production of several other chlorinated solvents, such as ethylene dichloride and 1,1,1-trichloroethane, also have the potential to produce HCB at trace levels.[14]

Process Description

During the production of carbon tetrachloride, trichloroethylene, and perchloroethylene, HCB is formed as a reaction byproduct from chlorination, oxychlorination, and cracking operations. Flow diagrams illustrating the main processes for producing carbon tetrachloride, trichloroethylene, and perchloroethylene are presented in Figures 19, 20, and 21. Potential HCB-containing waste streams are indicated in these figures. Hexachlorobenzene is usually found as a residue in the heavy ends or still bottoms during distillation or purification. The heavy, tarry residue also contains other chlorinated hydrocarbons in addition to HCB. Generally, these wastes are removed and stored in containers prior to their ultimate disposal by incineration.[14]

The HCB levels in production wastes vary greatly by chemical and by plant. This variability in the HCB concentration is related to the processes and feedstock materials used. Wastes generated by trichloroethylene production appear to contain the lowest levels of HCB. In general, it is difficult to quantify a typical HCB concentration in the process wastes.[14]

Emissions

The HCB generated by the production of the chlorinated solvents occurs as bottoms from distillation processes. When the HCB-containing waste is removed from the distillation unit, the HCB portion is essentially solid. Considering its physical state and the low vapor pressure of HCB at ambient temperatures (i.e., 20°C), the potential for fugitive HCB volatilization during waste generation and waste handling

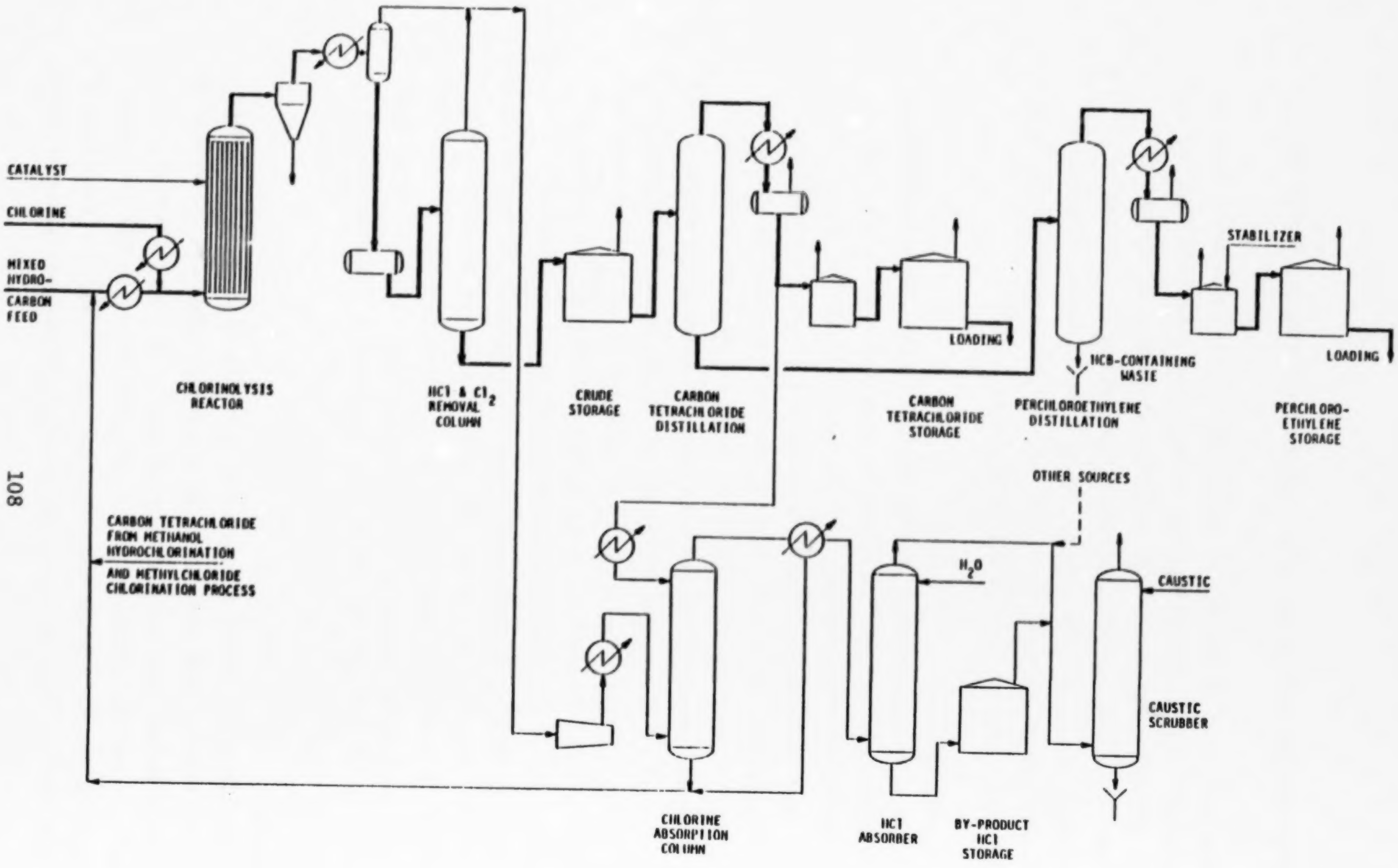

CATALYST
CHLORINE
MIXED HYDRO-CARBON FEED
CHLORINOLYSIS REACTOR
HCl & Cl_2 REMOVAL COLUMN
CRUDE STORAGE
CARBON TETRACHLORIDE DISTILLATION
CARBON TETRACHLORIDE STORAGE
LOADING
HCB-CONTAINING WASTE
PERCHLOROETHYLENE DISTILLATION
STABILIZER
PERCHLORO-ETHYLENE STORAGE
LOADING
CARBON TETRACHLORIDE FROM METHANOL HYDROCHLORINATION
AND METHYLCHLORIDE CHLORINATION PROCESS
OTHER SOURCES
H_2O
CAUSTIC
CAUSTIC SCRUBBER
CHLORINE ABSORPTION COLUMN
HCl ABSORBER
BY-PRODUCT HCl STORAGE

Figure 19. Process flow diagram for the production of carbon tetrachloride and perchloroethylene by hydrocarbon chlorinolysis.[14]

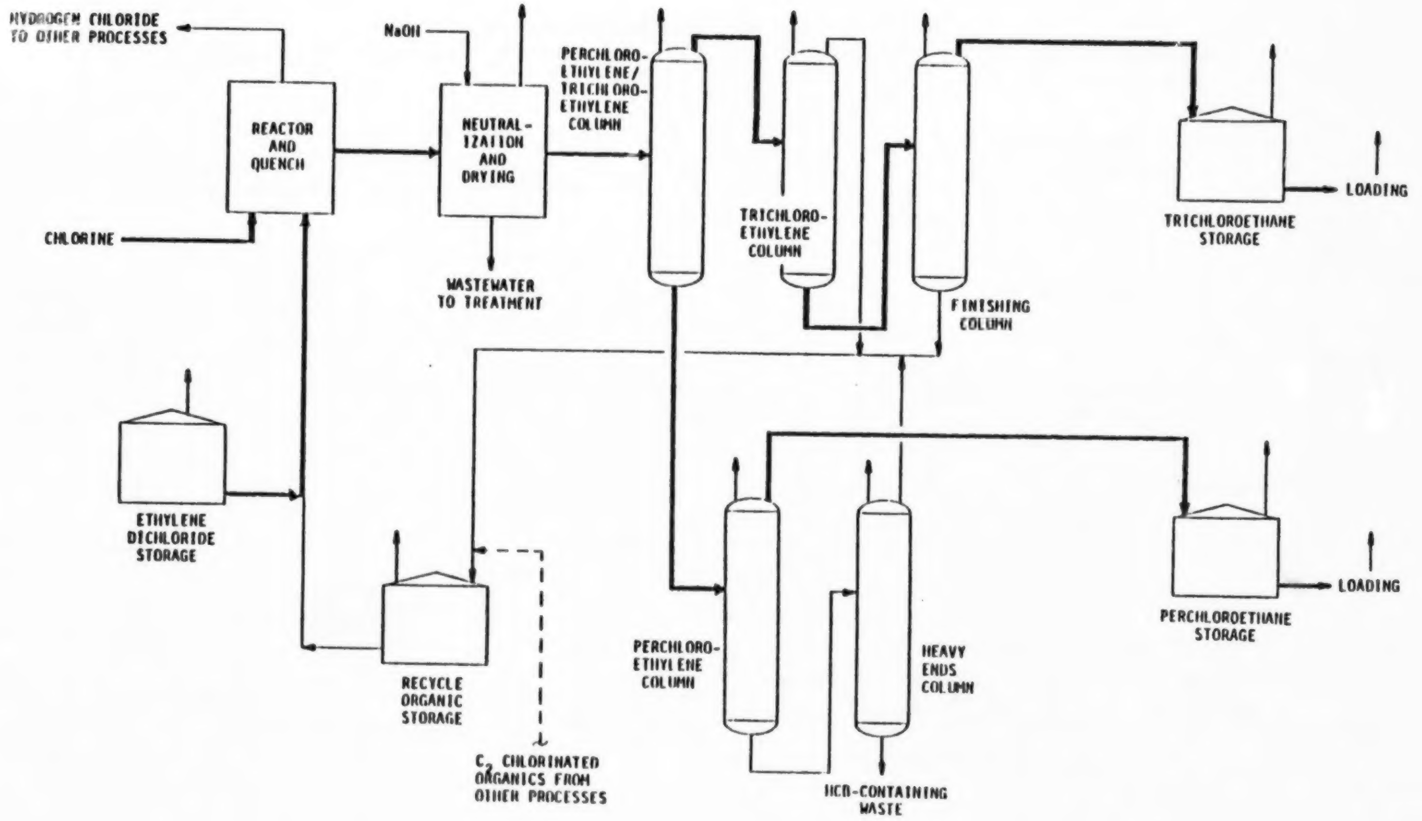

HYDROGEN CHLORIDE TO OTHER PROCESSES
NaOH
REACTOR AND QUENCH
NEUTRAL-IZATION AND DRYING
PERCHLORO-ETHYLENE/TRICHLORO-ETHYLENE COLUMN
CHLORINE
WASTEWATER TO TREATMENT
TRICHLORO-ETHYLENE COLUMN
FINISHING COLUMN
TRICHLOROETHANE STORAGE
LOADING
ETHYLENE DICHLORIDE STORAGE
RECYCLE ORGANIC STORAGE
C_2 CHLORINATED ORGANICS FROM OTHER PROCESSES
PERCHLORO-ETHYLENE COLUMN
HEAVY ENDS COLUMN
HCB-CONTAINING WASTE
PERCHLOROETHANE STORAGE
LOADING

Figure 20. Process flow diagram for the production of perchloroethylene and trichloroethylene by chlorination.[14]

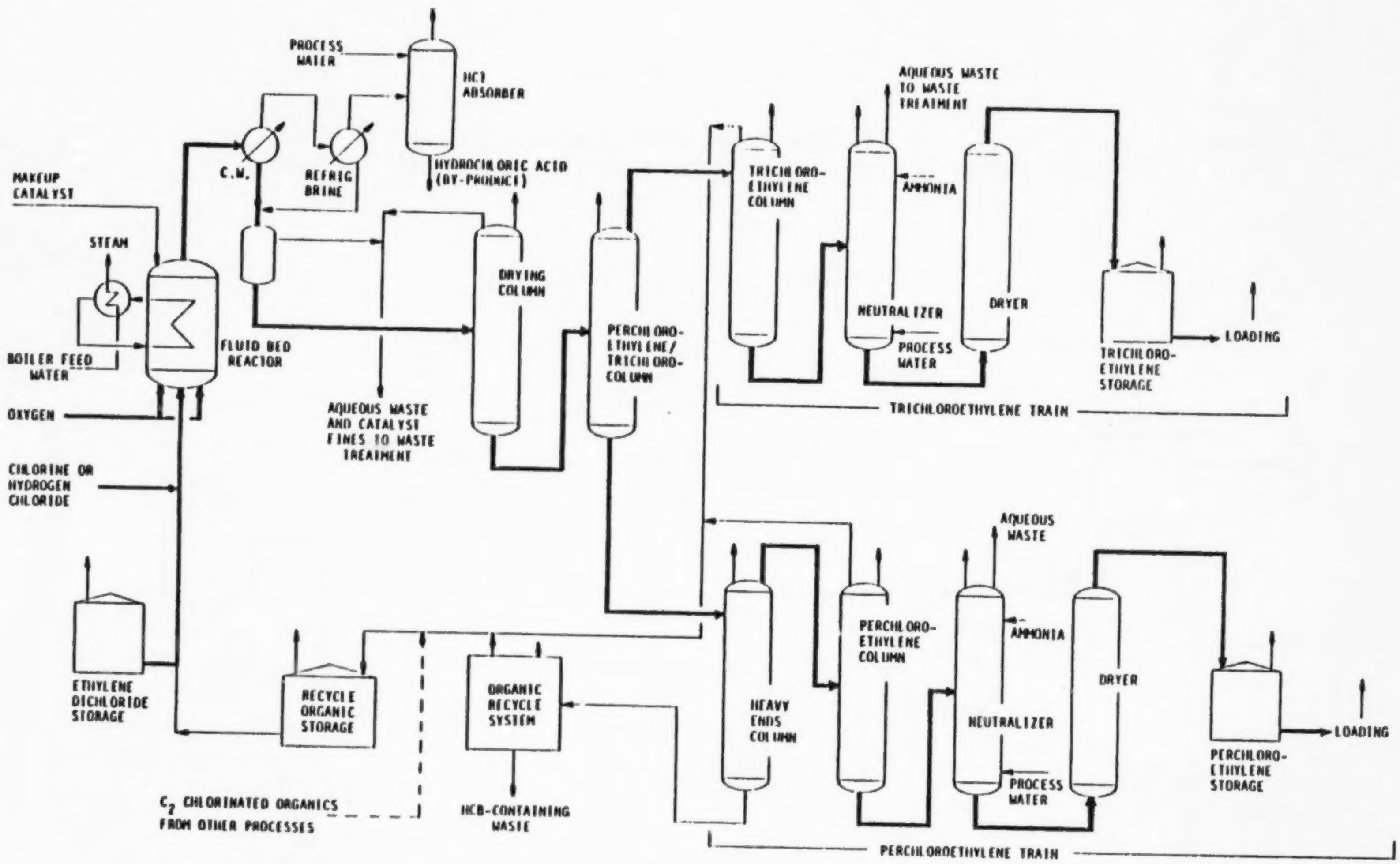

PROCESS WATER
HCl ABSORBER
HYDROCHLORIC ACID (BY-PRODUCT)
MAKEUP CATALYST
C.W.
REFRIG BRINE
STEAM
BOILER FEED WATER
FLUID BED REACTOR
OXYGEN
CHLORINE OR HYDROGEN CHLORIDE
DRYING COLUMN
AQUEOUS WASTE AND CATALYST FINES TO WASTE TREATMENT
PERCHLORO-ETHYLENE/ TRICHLORO-COLUMN
TRICHLORO-ETHYLENE COLUMN
AQUEOUS WASTE TO WASTE TREATMENT
AMMONIA
NEUTRALIZER
PROCESS WATER
DRYER
TRICHLORO-ETHYLENE STORAGE
LOADING
TRICHLOROETHYLENE TRAIN
ETHYLENE DICHLORIDE STORAGE
RECYCLE ORGANIC STORAGE
ORGANIC RECYCLE SYSTEM
HCB-CONTAINING WASTE
C2 CHLORINATED ORGANICS FROM OTHER PROCESSES
HEAVY ENDS COLUMN
PERCHLORO-ETHYLENE COLUMN
AQUEOUS WASTE
AMMONIA
NEUTRALIZER
PROCESS WATER
DRYER
PERCHLORO-ETHYLENE STORAGE
LOADING
PERCHLOROETHYLENE TRAIN

Figure 21. Process flow diagram for the production of perchloroethylene and trichloroethylene by oxychlorination.[14]

operations is minimal. Actual tests at a perchloroethylene plant have indicated that HCB waste handling operations are not a source of HCB air emissions. In these tests, neither uncontrolled air emissions associated with handling HCB-containing waste nor air emissions from waste storage tanks were found to contain HCB.[81]

In the past, waste storage piles at plants indirectly generating HCB may have been fugitive HCB emission sources due to slow evaporative losses. More recently, however, with the advent of the management and control of hazardous wastes under the Resource Conservation and Recovery Act (RCRA), the use of waste storage piles has greatly declined because of the stringent site containment and monitoring requirements in place for open piles. Most HCB waste generators currently store their wastes in containers prior to final disposal in incinerators or landfills.[81]

The majority of chlorinated solvent plants known to generate HCB wastes use incineration as a means of ultimate disposal, while a few utilize offsite landfill facilities (Table 23). Of the plants known to be incinerating their wastes, all but one, Diamond Shamrock, incinerate their wastes on the plant site. The plants operate RCRA approved incinerators which must be at least 99.99 percent efficient at destroying HCB. The offsite incinerator must meet the same RCRA requirements to be allowed to burn HCB. The ultimate HCB emission point from incinerating these wastes will not necessarily be the incinerator stack, but will probably be the stack on the caustic wet scrubber used to control hydrochloric acid (HCl) emissions from the incinerator.[81]

Source Locations

Currently known producers of carbon tetrachloride, trichloroethylene, and perchloroethylene and their methods of production are shown in Tables 24, 25, and 26. Most of the listed facilities reported HCB-containing wastes on their Resource Conservation and Recovery Act (RCRA) Part A applications on file with the EPA and State hazardous waste agencies.[81]

TABLE 23. SUMMARY OF DISPOSAL PRACTICES FOR HEXACHLOROBENZENE WASTES - 1984[81]

Plant	Location	HCB Waste Disposal Method
Dow Chemical	Freeport, TX	On-site Incineration
	Plaquemine, LA	On-site Incineration
	Pittsburg, CA	On-site Incineration
E.I. EuPont de Nemours	Corpus Christi, TX	Unknown
Diamond Shamrock	Deer Park, TX	Off-site Incineration
LCP Chemicals and Plastics	Moundsville, WV	Off-site Landfill
Stauffer Chemical	Louisville, KY,	Unknown[a]
PPG Industries	Lake Charles, LA	On-site Incineration
Vulcan Materials	Geismar, LA	On-site Incineration
	Wichita, KS	On-site Incineration
Olin Corporation	Leland, MS	Off-site Landfill
SDS Biotech	Greens Bayou, TX	Off-site Landfill
Velsicol Chemical	Memphis, TN	Off-site Landfill
	Marshall, IL	Off-site Landfill

[a] It is known that the plant does not have on-site landfilling or incineration.

Note: This listing is subject to change as market conditions change, facility ownership changes, plants are closed, etc. The reader should verify the existence of particular facilities by consulting current listings and/or the plants themselves. The level of chlorobenzene emissions from any given facility is a function of variables such as capacity, throughput and control measures, and should be determined through direct contacts with plant personnel.

TABLE 24. CHEMICAL PRODUCERS OF CARBON TETRACHLORIDE - 1984[82]

Company Location	Method of Production
Dow Chemical Freeport, Texas	Methane chlorination and chlorinolysis of mixed hydrocarbons with perchloroethylene co-product
Pittsburg, California	Methane chlorination and chlorinolysis of mixed hydrocarbons with perchloroethylene co-product
Plaquemine, Louisiana	Chlorinolysis of mixed hydrocarbons with perchloroethylene co-product
E.I. DuPont de Nemours Ingleside, Texas	Methane and ethylene chlorination with perchloroethylene co-product
LCP Chemicals and Plastics Moundsville, West Virginia	Methyl chloride chlorination and methane chlorination
Stauffer Chemical	
Louisville, Kentucky	Methane chlorination
LeMoyne, Alabama	Carbon disulfide chlorination
Vulan Materials Geismar, Louisiana	Chlorinolysis of mixed hydrocarbons with perchloroethylene co-product
Wichita, Kansas	Methyl chloride and methane chlorination, chlorinolysis of mixed hydrocarbons with perchloroethylene co-product

Note: This listing is subject to change as market conditions change, facility ownership changes, plants are closed, etc. The reader should verify the existence of particular facilities by consulting current listings and/or the plants themselves. The level of chlorobenzene emissions from any given facility is a function of variables such as capacity, throughput and control measures, and should be determined through direct contacts with plant personnel.

TABLE 25. CHEMICAL PRODUCERS OF TRICHLOROETHYLENE - 1984[83]

Company Location	Method of Production
Dow Chemical Freeport, Texas	Chlorination of ethylene dichloride
PPG Industries, Inc. Lake Charles, Louisiana	Oxychlorination of ethylene dichloride

Note: This listing is subject to change as market conditions change, facility ownership changes, plants are closed, etc. The reader should verify the existence of particular facilities by consulting current listings and/or the plants themselves. The level of chlorobenzene emissions from any given facility is a function of variables such as capacity, throughput and control measures, and should be determined through direct contacts with plant personnel.

TABLE 26. CHEMICAL PRODUCERS OF PERCHLOROETHYLENE - 1984[84]

Company Location	Method of Production
Diamond Shamrock Deer Park, Texas	Chlorination of ethylene dichloride
Dow Chemical Freeport, Texas[a]	Chlorinolysis of mixed hydrocarbons producing carbon tetrachloride as a co-product
Pittsburg, California	Chlorinolysis of mixed hydrocarbons producing carbon tetrachloride as a co-product
Plaquemine, Louisiana	Chlorinolysis of mixed hydrocarbons producing carbon tetrachloride as a co-product
E.I. DuPont de Nemours Corpus Christi, Texas	Not available
PPG Industries, Inc. Lake Charles, Louisiana	Chlorination of ethylene dichloride
Stauffer Chemical Louisville, Kentucky[a]	Chlorinolysis of mixed hydrocarbons producing carbon tetrachloride as a co-product
Vulcan Materials .Geismar, Louisiana	Chlorinolysis of mixed hydrocarbons producing carbon tetrachloride as a co-product
Wichita, Kansas	Chlorinolysis of mixed hydrocarbons producing carbon tetrachloride as a co-product

[a] Plants on standby.

Note: This listing is subject to change as market conditions change, facility ownership changes, plants are closed, etc. The reader should verify the existence of particular facilities by consulting current listings and/or the plants themselves. The level of chlorobenzene emissions from any given facility is a function of variables such as capacity, throughput and control measures, and should be determined through direct contacts with plant personnel.

HEXACHLOROBENZENE GENERATION DURING PESTICIDE, HERBICIDE, AND FUNGICIDE PRODUCTION

The production of aromatic chlorinated hydrocarbon pesticides, herbicides, and fungicides has been indicated in the literature to generate HCB wastes. In total, pesticide production accounts for about 40 percent of the HCB generated in the United States. The bulk of HCB from pesticide production is associated with two compounds: the fungicide pentachloronitrobenzene (PCNB) and the herbicide dimethyl tetrachloroterephthalate (DCTA), or Dacthal•. The production of another pesticide, chlorothalonil or Daconil•, is also expected to generate HCB wastes.[15]

Process Descriptions

Pentachloronitrobenzene ($C_6Cl_5NO_2$) is produced by chlorinating various chloronitrobenzenes in the presence of an iron-iodine catalyst. As with other HCB-generating processes, HCB from PCNB production is expected to occur in distillation bottoms.[15] No further information is available concerning the production process.

The production of Dacthal• involves the reaction of hexachloro-p-xylene with terephthalic acid, followed by the chlorination of the crude reaction product to form tetrachloroterephthaloyl dichloride. Reactions during the chlorination process form HCB. The chlorination product then undergoes esterification to produce Dacthal•. HCB is a component of the solid waste streams generated by this process. In 1975, HCB was reported to constitute 84 percent of wastes from Dacthal• production; however, no information is available concerning current levels of HCB in production wastes.[15]

All data relating to the production of Daconil• and quantities of HCB generated are confidential because there is only a single producer of the compound. However, the production of this chemical has not been discussed in the literature as being an HCB source, and it is believed that the quantities of HCB generated are small in comparison to those from PCNB and Dacthal•.

Emissions

HCB air emissions from pesticide production result primarily from the final waste disposal activities used to treat the HCB wastes. HCB wastes from pesticide production are disposed of in off-site landfills. As a result, HCB emissions from landfills can occur from volatilization and windblown and physical displacement of soil particles containing adsorbed HCB.[81] Current waste practices for HCB waste-producing plants appear in Table 23.

The above pesticides contain HCB as a contaminant and will be released upon use.[81]

Source Locations

The only facility currently producing PCNB is Olin Corporation in Leland, Mississippi. Dacthal® and Daconil® are manufactured by SDS Biotech (formerly Diamond Shamrock) in Green Bayou, Texas.[15] This listing is subject to change as market conditions change, facility ownership changes, plants are closed, etc. The reader should verify the existence of particular facilities by consulting current listings and/or the plants themselves. The level of HCB emissions from any given facility is a function of variables such as capacity, throughput and control measures, and should be determined through direct contacts with plant personnel.

USE OF FUNGICIDES AND HERBICIDES CONTAINING HEXACHLOROBENZENE

HCB will be released to the environment through the use of an HCB product or the use of a material containing HCB as a contaminant.

The only product line in use in the United States containing HCB as an active ingredient is a group of fungicides used as seed treatments (Table 27). Since these seed treatments are applied as liquids, some potential for fugitive HCB volatilization exists during application. Subsequent volatilization of HCB from the treated seeds may also be a source of HCB emissions. Due to recent EPA cancellation of the registration of these HCB treatment fungicides, their use should cease after existing inventories are depleted.[81]

The most important source of HCB air emissions appears to be the use of PCNB, Dacthal®, and Daconil®, which contain HCB as a trace contaminant. PCNB is a fungicide mainly used as a soil and seed treatment for cotton, peanuts, and turf. Dacthal® is a herbicide treatment for soils used to grow vegetables, field crops, strawberries, nursery stock and turf. No specific uses of Daconil® were found in the literature. These compounds are used in much greater quantities and on a much wider variety of materials than the chemicals containing HCB as an active ingredient. No effort has been made to reduce or ban the use of PCNB, Dacthal®, or Daconil®. Fugitive HCB air emissions could potentially occur from the application of these chemicals due to volatilization and windblown displacement of soil containing adsorbed HCB. HCB emissions of this type could occur in any region of the country because PCNB, Dacthal®, and Daconil® are applied in agricultural areas nationwide.[81]

TABLE 27: PREVIOUSLY REGISTERED SEED TREATMENT FORMULATIONS CONTAINING HEXACHLOROBENZENE[16,a]

- Ortho Wheat Seed Protectant (Slurry)
- Ortho Drill Box Wheat Seed Protectant
- Ortho HCB 4 Flowable Seed Protectant
- No Bunt "40"
- Rhodia No Bunt Liquid
- Hexachlorobenzene (Technical Grade)
- Captan-Hexachlorobenzene 40-40 Seed Protectant
- Captan-Hexachlorobenzene 20-20 Seed Protectant
- Captan-HCB-Maneb 20-20-20 Seed Protectant
- Captan-Hexachlorobenzene 40-10 Seed Protectant
- Agsco DB-Yellow-A Seed Disinfectant
- Miller's Smut-Go
- Res-Q Seed Disinfectant Powder
- Dual Purpose Res-Q
- Res-Q-100 Seed Disinfectant and Protectant Dust or Slurry
- Res-Q-200 Seed Disinfectant and Protectant Dust or Slurry
- Parsons Seed Saver-DB
- Granox N-M Fungicide Seed Treatment
- Granox Flowable Seed Treatment
- Seed Shield Maneb/HCB Flowable
- Seed Shield Maneb-HCB Planter Box Seed Treater
- Thihex
- Sowmatic I
- Clean Crop M50-H10 Seed Protectant for Small Grains
- Seed-Treat Drill Box & Slurry #40
- Clean Crop HCB Seed Treater
- Maneb-HCB Planter Box Seed Treater

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[a] Registrations for these compounds have been cancelled by EPA as of 1984.[85] Upon cancellation it is a violation of FIFRA to further produce or use the compounds after existing inventories are depleted.

VOLITILIZATION OF CHLOROBENZENES FROM WASTEWATER TREATMENT OPERATIONS

Chlorobenzenes may be emitted when wastes containing chlorobenzenes are present in surface impoundments for treatment and storage of wastewater or in open treatment and storage tanks. Treatment and storage facilities may be located at the site of generation of the waste, or at a separate commercial waste treatment plant. In addition, publicly owned treatment works (POTWs) may emit chlorobenzenes if they receive wastewaster from plants producing chlorobenzenes either as a main product or as a byproduct, or from plants using chlorobenzenes as an intermediate. For example, at one 42 million gallon per day (MGD) POTW, 93, 61 and 100 percent, respectively, of the influent contributions of 1,2,4-TCB, m-DCB, and p-DCB were found to have originated as byproducts of industrial processes. Moreover, at this plant, approximately 54 percent of the volatile organics (including MCB) were attributed to industrial origins.[86]

A typical secondary treatment facility sequence utilized by many existing wastewater treatment facilities consists of screening, grit removal, primary clarification, conventional activated sludge with aeration, and chlorination. Due to the volatile nature of chlorobenzenes, air emissions are expected mainly from clarification and aeration processes. Measurements of the chlorobenzenes concentrations in the effluent of the 42 MGD POTW discussed above suggest that the overall treatment process removes 40 to 90 percent of the incoming chlorobenzenes, primarily during activated sludge aeration. Partitioning of 1,2,4-TCB, m-DCB, and p-DCB to the primary clarifier sludge and activated sludge indicates that some fraction of these pollutants may accumulate onto settleable or floatable solids. However, the remainder is expected to be removed by either air stripping or by biodegradation.[86] Air stripping would result in air emissions of chlorobenzenes.

Testing of the aeration basins at a small municipal treatment plant (handling 40 percent industrial and 60 percent municipal sewage) resulted in the measurement of emissions of o-DCB and m-DCB ranging from levels of 148 to 478 grams/hour and 155 to 609 grams/hour, respectively.[87] Monochlorobenzene was measured only at trace quantities. No data were collected for other chlorobenzenes. Too little data are available to extrapolate these test results to other wastewater treatment plants.

Source Locations

Specific locations of POTWs that treat wastewater containing VDC were not identified, therefore the reader should contact particular facilities to determine if such wastes are treated. For the locations of industrial facilities handling VDC wastes, refer to separate sections on production processes where VDC is produced or used as a feedstock.

BURNING OF WASTE OIL

Monochlorobenzene and o-dichlorobenzene have been identified as contaminants of potential concern in waste crankcase oils used as fuel. Approximately 1.2 billion gallons of used automotive and industrial oils are generated annually of which 35 percent is collected and used as fuel.[88] Studies of waste oil composition show that waste industrial oils are contaminated with chlorinated solvents. It has also been suggested that chlorinated hydrocarbons in the oils are formed chemically during oil use or may result from contamination by solvents in holding tanks. Observed concentration ranges for MCB and o-DCB in waste oils are 4 to 500 ug/l and 60 to 160 ug/l, respectively.[88]

Emissions

It is uncertain how much MCB and o-DCB are released into the atmosphere during the burning of waste oil as fuel. Emissions are related to initial concentrations of chlorobenzene in the waste oil as well as boiler operating parameters and control devices. No information was available concerning actual emission rates.

Source Locations

Locations of boilers which use waste oils for fuel have not been identified in the literature.

MISCELLANEOUS USES OF CHLOROBENZENES

The following section discusses miscellaneous uses of chlorobenzenes in production for which no detailed information is available. Also included are possible uses and emission sources for less commonly used chlorobenzenes not previously discussed, namely, m-DCB, 1,2,3-TCB and 1,3,5-TCB.

Monochlorobenzene

MCB is used consumptively as an inert process solvent in the production of rubber intermediate and during diisocyanate manufacture. As an inert process solvent, MCB is the medium in which the process reaction occurs and is later separated for recovery and recycling. Nonrecoverable solvent and impurities are released primarily in water discharges, with a small quantity emitted to the atmosphere.[11]

MCB is employed as a solvent in the production of adhesives, paints, polishes, and waxes. The exact function of solvent use is not known, however, it is estimated that a majority of MCB is retained in the product and will be released through subsequent use.[11]

Until recently, Monsanto Company utilized large quantities of monochlorobenzene in its popular pesticide, Lasso®. Since then, Monsanto has reformulated the pesticide from a liquid to a new encapsulated version which will ultimately lower Monsanto's MCB use by 80 percent. No information was available concerning processes or emissions.[89]

o-Dichlorobenzene

Like p-DCB, o-DCB is also used as a deodorant; however, due to its liquid form it is distributed in a different manner.[11] Literature cites its use in wastewater treatment for this purpose, although details were not disclosed for actual usage.

p-Dichlorobenzene

Lesser known uses of p-DCB include its use in the manufacture of pharmaceuticals, floor waxes and finishes, as a chemical intermediate, and as an extreme pressure lubricant.[11] Para-dichlorobenzene is present as a contaminant in the above substances and may be released through subsequent use.

m-Dichlorobenzene

The use of m-DCB is not extensive, although it has been used as a fumigant and insecticide. Due to its limited use, emissions contributed by these sources are negligible.[11]

1,2,4-Trichlorobenzene

1,2,4-TCB is used as a solvent for crystallization of high melting point products, in termite control, in septic tank and drain cleaner preparations, and as a lubricant. Further information on the above uses is not available. Emissions are given off during production and use of secondary products.[11]

1,3,5-Trichlorobenzenes

1,3,5-TCB is also used as a solvent for high temperature melting point products in addition to uses as a coolant in electrical installations and glass tempering, heat transfer medium, lubricant, and synthetic transformer oil. It is used in termite preparations, the manufacture of 2,5-dichlorophenol, polyester dyeing and insecticides. It is estimated that emissions are released during the production and use of these products.[11,39]

1,2,3-Trichlorobenzenes

The limited uses of 1,2,3-TCB include its use as an organic intermediate, termite control agent, agricultural insecticide, and synthetic transformer oil. Emissions are expected from termite control operations, agricultural runoff, general laboratory usage and from its use as a transformer oil.[11]

Hexachlorobenzene

HCB solid wastes are generated during the synthesis of hexachlorocyclopentadiene (HCCPD), a chemical intermediate used to make pesticides and flame retardants. Currently, Velsicol Chemical operates two HCCPD-generating facilities located in Marshall, Illinois, and Memphis, Tennessee (subject to change as market conditions change, facility ownership changes, plants are closed, etc.).[16] Wastes generated in the distillation bottoms contain 2 to 6 percent HCB, and are landfilled, potentially resulting in volatilization during waste handling.[81]

HCB wastes are also known to have been generated during past electrolytic chlorine production and sodium chlorate production processes which used graphite anodes containing coal tar pitch binder. Since then almost all graphite anodes have been replaced with metal anodes in these operations.[16]

Industrial uses of HCB have declined in recent years. Currently no HCB is produced domestically or imported into the United States. Of importance only from a historical standpoint, past uses of HCB include (1) as a porosity agent in the manufacture of industrial graphite anodes; (2) as a fluxing agent in smelting operations of primary aluminum production; (3) as a peptizing agent in the manufacture of nitros and styrene rubbers, and (4) as a feedstock in production of pyrotechnic (e.g., signal flares) and ordnance (e.g., tracer bullets) materials for military and civilian applications.

SECTION 5

SOURCE TEST PROCEDURES

Chlorobenzene emissions can be measured using EPA Reference Method 23, which was proposed in the Federal Register on June 11, 1980.[90] The method has not been validated by EPA for chlorobenzenes but a similar analytical procedure has been used to measure occupational exposures to chlorobenzenes.

In Method 23, a sample of the exhaust gas to be analyzed is drawn into a Tedlar® or aluminized Mylar® bag as shown in Figure 22. Tedlar® is considered a more reliable bag material than Mylar® for chlorobenzenes. The bag is placed inside a rigid leak proof container and evacuated. The bag is then connected by a Teflon® sampling line to sampling probe (stainless steel, Pyrex® glass, or Teflon®) at the center of the stack. Sample is drawn into the bag by pumping air out of the rigid container.

The sample is then analyzed by gas chromatography (GC) coupled with flame ionization detection (FID). Analysis should be conducted within one day of sample collection. The recommended GC column is 3.05 m by 3.2 mm stainless steel, filled with 20 percent SP-2100/0.1 percent Carbowax 1500 on 100/120 Supelcoport. This column normally provides an adequate resolution of halogenated organics. (Where resolution interferences are encountered, the GC operator should select the column best suited to the analysis.) The column temperature should be set at 100°C. Zero helium or nitrogen should be used as the carrier gas at a flow rate of approximately 20 ml/min.

The peak area corresponding to the retention time of chlorobenzenes is measured and compared to peak areas for a set of standard gas mixtures to determine the chlorobenzene concentration. The range of the method is 0.1 to 200 ppm; however, the upper limit can be extended by extending the calibration range or diluting the sample. To avoid

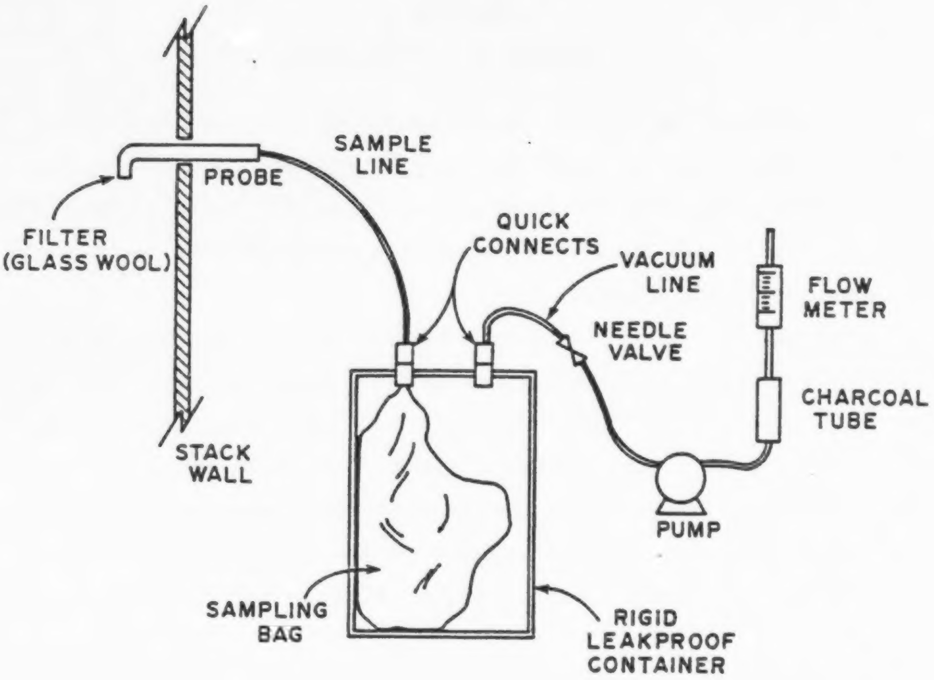

Figure 22. Method 23 Sampling Train.[90]

absorption of chlorobenzenes by the Tedlar® bag, the sample should be analyzed as soon as possible after collection, preferably on the same day. The method does not apply when chlorobenzenes are contained in particulate matter.

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